

THE THERMODYNAMIC PROPERTIES OF SULPHONATED POLYSTYRENE EXCHANGERS SATURATED WITH A SINGLE CATION

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Summary

If an ion exchanger is treated as if it were an aqueous electrolyte, it is possible to use several independent experimental data to calculate the osmotic and activity coefficients of the resin phase. Illustrative examples are quoted. The activity coefficient of pure sodium "resinate" is calculated with satisfactory agreement from isopiestic data, and by two methods from the sodium-hydrogen exchange reaction. Activity coefficient curves for lithium, sodium, potassium, rubidium, caesium, copper, and barium "resinates" are given and also activity coefficient data for a number of other divalent cationic "resinates", at a single value of the ionic strength. These activity coefficients show similar trends to those of aqueous electrolytes.

I. INTRODUCTION

In the previous paper (Duncan 1955) it has been shown that information about the ionic state of the components of an ion exchange resin can be deduced from a statistical mechanical consideration of the temperature dependence of the equilibrium between an ion exchanger and an aqueous solution. Unfortunately, remarkably few data are available on the temperature dependence of ion exchange reactions, compared with the numerous ion exchange equilibria which have been investigated under isothermal conditions. Whilst a clear picture of the behaviour of the individual ions cannot be obtained from such data alone, the free energy changes do provide useful information about ionic interaction. As an essential step in interpreting the free energy changes, this paper describes the different methods by which the activity coefficients of pure exchangers may be calculated from experimental data, many of which are already available in the literature.

If a cation exchanger of the sulphonated polystyrene type is placed in an aqueous solution containing either a single or two cationic species, the distribution of cations and neutral electrolyte between the two phases can be satisfactorily described by assuming the exchanger to be an electrolyte (e.g. sodium "resinate") dissolved in the swelling water normally taken up by the exchanger when in contact with aqueous solutions (Duncan 1952; Glueckauf 1952). In earlier work v , the number of g ions per mole of dissociated resinate, was taken as unity (Duncan 1952; Glueckauf 1952) on the grounds that it seemed to be

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tending to this value at zero concentration. Recent work by Gregor *et al.* (1952) and Waxman, Sundheim, and Gregor (1953) has suggested that such a procedure is unrealistic. We are clearly not justified in ascribing any firm physical interpretation to a value of ν of unity, but this does not affect any of the relationships calculated on such an assumption. It merely means that $\nu\bar{\varphi}$ must be inserted for any value of $\bar{\varphi}$ previously calculated. With this reservation in mind, therefore, we shall still continue, for simplicity, to treat the resin as if it were a simple electrolyte, with the thermodynamic data referred to a standard state of pure water. The empirical relations and experimental methods quoted here will still be valid, but the values of $\bar{\gamma}$ and $\bar{\varphi}$ must now be assumed to take up any uncertainties in the value of ν .

In assessing ionic interaction in mixed exchangers, one is usually more interested in the activity coefficient than in the osmotic coefficient. As the two are interdependent, however, the second may be assessed by any experimental procedure which determines the first. Several methods of determining osmotic data are enumerated below. Procedures for obtaining activity coefficients, both from osmotic coefficients and by other means, are discussed later. The experimental techniques for determining mass products and water uptake were identical with those described earlier (Duncan and Lister 1949; Duncan 1952).

II. DETERMINATION OF THE OSMOTIC COEFFICIENT OF A METAL RESINATE

All the methods discussed below depend on the use of the fundamental equation describing the water distribution between the exchanger and an external phase, namely,

$$\ln a_w - \ln \bar{a}_w = P v_w / RT, \quad \dots \dots \dots (1)$$

where a_w and \bar{a}_w are the water activities in the external phase, and in the exchanger respectively. The latter is usually indicated by a superscript bar. P is the "swelling" pressure, and v_w the molar volume of the water. The osmotic coefficient $\bar{\varphi}$ is expressed in terms of the water activity for all cation types by the usual relation

$$\ln \bar{a}_w = -0.018 [\bar{M}\bar{R}] \bar{\varphi}, \quad \dots \dots \dots (2)$$

where $[\bar{M}\bar{R}]$ is the concentration of the metal "resinate" in the pure form expressed in moles of cation/1000 g swelling water. Hence, knowing \bar{a}_w , $\bar{\varphi}$ can be evaluated.

(a) Method A: From Isopiestic Data

This method, which has been described in detail earlier (Glueckauf 1952), depends on determining the water content (and hence the concentration) of an ion exchanger of low cross-linking in equilibrium with a given vapour pressure of water. Hence, $\bar{\varphi}$ may be obtained when a_w is known, since P is small enough to neglect. No new results on this method are presented here. But, in cases where the general form of the swelling-pressure curve is known (e.g. with sulphonated cross-linked polystyrene) or the right-hand side of equation (1) is small enough to be neglected (say with less than 5 per cent. divinyl benzene), $\bar{\varphi}$ may also be estimated by methods *B* and *C* below.

(b) *Method B: From Isopiestic Data on Exchangers of High Cross-Linking*

Most of the commercial ion exchangers of this type contain about 10 per cent. divinyl benzene as cross-linking agent, for which the variation of swelling pressure with ion equivalent volume is now well established (Glueckauf 1952). The right-hand side of equation (1) can thus be estimated with reasonable accuracy and both \bar{a}_w and $\bar{\varphi}$ may be evaluated by determining the water content of the exchanger in equilibrium with a given water vapour pressure. Such an exchanger will not swell indefinitely, so that the osmotic coefficient cannot be determined at a concentration in the exchanger less than that which exists when the exchanger is in pure water ($a_w=1$). But since in practice one is seldom interested in lower concentrations in ion exchange reactions this limitation is not serious. As an example of the method, Table 1 shows the osmotic coefficients at 15 °C of copper resins at different concentrations, which have been determined from isopiestic experiments on "Dowex 50", and evaluated, using the relation

$$\bar{\varphi} = \left[\frac{Pv_w}{RT} - \ln \left\{ \frac{p}{p_0} \right\} \right] / 0.018[\overline{MR}], \quad \dots \dots \dots (3)$$

where p is the water vapour pressure, and p_0 the saturation vapour pressure at the same temperature. The swelling pressure P was interpolated from previous data (Glueckauf 1952). It should be added that, even with exchangers of high cross-linking, the swelling pressure term becomes small enough to be neglected at high exchanger concentrations (i.e. low partial vapour pressures).

TABLE 1
CALCULATION OF $\bar{\varphi}_{\text{Cu}}^0$ FROM ISOPIESTIC DATA ON "DOWEX 50"

$-\text{Log } a_w$	$[\text{CuR}]$	P	$\bar{\varphi}_{\text{Cu}}^0$
0.004	4.81	62	2.64
0.151	5.85	5	3.30
0.260	6.63	—	5.01
0.649	14.01	—	5.92
0.957	18.71	—	6.54

(c) *Method C: From the Water Content of an Exchanger Immersed in Water*

If an ion exchanger is immersed in pure water (and hydrolysis or solution of the resin can be taken as negligible), equation (1) becomes

$$\ln \bar{a}_w = -0.018[\overline{MR}]\bar{\varphi} - Pv_w/RT. \quad \dots \dots \dots (4)$$

Since the water content of the exchanger is given by the difference in weight of the oven-dried and the wet (surface-dried) exchanger, $[\overline{MR}]$ may easily be obtained if the exchange capacity is known. Thus, since P is known for a given resin equivalent volume, $\bar{\varphi}$ may in principle be computed from the data obtained in a very simple experiment. The accuracy of such a procedure depends on the accuracy of assessment of the value of P , particularly when the cross-linking is high. When the cross-linking is unknown, it is necessary to evaluate P by

determining the water content of exchangers of different cation type with known osmotic properties; the ion equivalent volume of the resin must also be known (Table 2). Thus the osmotic coefficients of exchangers saturated with hydrogen, lithium, sodium, potassium, and silver are already well known (Glueckauf 1952). By determining the water content of an exchanger of unknown cross-linking ("Dowex 50") in these different ionic forms, $[\overline{MR}]$ and hence $\bar{\varphi}$ and P were evaluated for different values of V_R , the resin equivalent volume.

TABLE 2
EVALUATION OF P FOR AN EXCHANGER OF UNKNOWN CROSS-LINKING

Ion Type	$[\overline{MR}]$	$\bar{\varphi}$ (interpolated from Fig. 1, Glueckauf 1952)	P (atm) (calc. from eqn. (4))	V_R
H	6.21	1.62	241	286
Li	6.53	1.42	220	281
Na	7.21	0.97	159	266
Ag	10.82	0.33	92	229

These values of P were plotted against V_R from which the appropriate P values were interpolated for use with data determined with the exchangers in other cation forms, the osmotic coefficients of which are tabulated in Table 3. In view of uncertainties in the values of $[\overline{MR}]$ (obtained from isopiestic data), the osmotic coefficients quoted are probably not accurate to better than ± 10 per cent. in this example.

TABLE 3
CALCULATION OF OSMOTIC COEFFICIENTS FROM THE WATER CONTENT OF PURE METAL FORMS OF AN EXCHANGER OF UNKNOWN CROSS-LINKING

Ion	$[\overline{MR}]$	V_R	P	$\bar{\varphi}$
Rb	8.17	261	152	0.78
Cs	9.24	259	144	0.65
Be	3.30	269	181	2.12
Mg	3.15	268	180	2.20
Ca	3.60	262	153	1.63
Sr	3.71	260	151	1.57
Ba	4.82	249	131	1.05
Cd	3.37	276	202	2.30
Co	3.23	269	180	2.24
Ni	3.38	267	178	2.12
Mn	3.19	262	153	1.86
Zn	3.02	284	236	3.00

This technique gives only a single value of $\bar{\varphi}$ for each exchanger. For a complete osmotic curve it is necessary to utilize exchangers of different cross-linking. The method is nevertheless straightforward, and is useful for rapidly checking the values obtained by other procedures.

(d) Method D: From the Change in Volume of an Exchanger in Dilute Salt Solution

The change in volume of an exchanger when immersed in an aqueous solution of a salt of the same cation may be determined either by direct observation with a microscope or from the change in water content of the exchanger by direct weighing of the surface-dry resin (with a small correction to make allowance for the uptake of neutral salt). Assuming the change in volume to be entirely due to loss of water from the exchanger, we may calculate $d[\overline{MR}]/da_w$ at $a_w=1$, the limiting value of the change in resin concentration for a unit change in water activity. Knowing the resin equivalent volume in pure water, we may also calculate $d[\overline{MR}]/dP$ from previous data (Glueckauf 1952). The osmotic coefficient of the pure exchanger $\overline{\varphi}_M$ may then be estimated using the following relations.

When an ion exchanger is equilibrated with a solution of a salt of a common cation we may write

$$\frac{P}{RT} + 2[MX]_{\varphi_{MX}} + [\overline{MR}] + 2 \cdot 3 \alpha_{12} [\overline{MR}] ([\overline{MX}] + [\overline{MR}]) - 2([\overline{MX}] + [\overline{MR}]) \overline{\varphi}_{MX}^0 = 0, \quad (5)$$

where MX refers to the aqueous electrolyte, α_{12} is the constant of a Harned type relation, the bars refer to the resin phase, and $\overline{\varphi}_{MX}^0$ is the osmotic coefficient of the electrolyte in a pure aqueous solution at the same ionic strength as that existing in the exchanger (see eqn. (3.5), Duncan 1952. This equation is in error, eqn. (5) above is correct). If \overline{MX} is small with respect to \overline{MR} , then

$$\frac{P}{RT} + 2[MX]_{\varphi_{MX}} + [\overline{MR}] + 2 \cdot 3 \alpha_{12} [\overline{MR}]^2 - 2[\overline{MR}] \overline{\varphi}_{MX}^0 = 0. \quad (6)$$

Differentiating with respect to \overline{MR} , we get

$$\frac{1}{RT} \left[\frac{dP}{d[\overline{MR}]} \right] + \frac{2d([\overline{MX}]_{\varphi_{MX}})}{d[\overline{MR}]} + 1 + 4 \cdot 6 \alpha_{12} [\overline{MR}] - 2 \overline{\varphi}_{MX}^0 - 2[\overline{MR}] \frac{d\overline{\varphi}_{MX}^0}{d[\overline{MR}]} = 0. \quad (7)$$

Also when $[MX]=0$ we have (eqn. (2.28), Duncan 1952)

$$\overline{\varphi}_{MR}^0 = 2 \overline{\varphi}_{MX}^0 - 2 \cdot 3 \alpha_{12} [\overline{MR}] - 1. \quad (8)$$

Combining (7) and (8) we arrive at

$$\overline{\varphi}_{MR}^0 = \overline{\varphi}_{MX}^0 - \frac{1}{2} + \frac{1}{2RT} \frac{dP}{d[\overline{MR}]} + \frac{d([\overline{MX}]_{\varphi_{MX}})}{d[\overline{MR}]} - [\overline{MR}] \frac{d\overline{\varphi}_{MX}^0}{d[\overline{MR}]} \quad (9)$$

The third and fourth terms of this expression for $\overline{\varphi}_{MR}^0$ can be determined by experiments of the above type. The first and last terms can be evaluated either from tabulated data, or from empirical relations of the type

$$\overline{\varphi}_{MX}^0 = 1 - 0 \cdot 15 [MX]^{\frac{1}{2}} + 1 \cdot 15 a [MX], \quad (10)$$

(where a is a constant) which is accurately obeyed by most electrolytes at high concentrations. Thus, $\overline{\varphi}_M^0$ the osmotic coefficient of the pure resinate may be

evaluated. Table 4 gives some osmotic coefficients which have been determined in this way from (a) swelling data determined (Duncan and Lister 1949) by microscopic observation ("Dowex 50" Na form) and (b) data on the water content of exchangers immersed in different salt solutions, quoted by Gregor, Guttoff, and Bregman (1951).

TABLE 4
CALCULATION OF OSMOTIC COEFFICIENTS FROM SWELLING DATA

Resin	Aqueous Electrolyte	[MR]	$\bar{\varphi}_M^0$ (calc.)	$\bar{\varphi}_M^0$ (from Fig. 1, Glueckauf 1952)	
"Dowex 50" Na form	NaCl	7.06	1.0 ± 0.20	0.85	
"Dowex 50" H form	HCl	9.36	2.49 ± 0.30	2.25	Calc. from results of Gregor <i>et al.</i> (1952)
NH ₄ form "DVB2"	NH ₄ Cl	1.49	0.60 ± 0.25		
NH ₄ form "DVB6"...	NH ₄ Cl	5.36	0.73 ± 0.25		
NH ₄ form "DVB10"	NH ₄ Cl	12.35	0.84 ± 0.25		

The lack of precision on the calculated values of $\bar{\varphi}_M^0$ is due (a) to the uncertainty in the evaluation of $dP/d[\bar{M}\bar{R}]$ arising because the degree of cross-linking is known only approximately and (b) to experimental inaccuracies. This is reflected in the limits quoted. But even if such discrepancies were real, they would not affect the validity of the method which rests on theoretically derived equations. The determination of

$$\frac{dP}{d[\bar{M}\bar{R}]_{[MX]=0}} \quad \text{and} \quad \left[\frac{d\{[\bar{M}\bar{X}]\bar{\varphi}_{MX}\}}{d[\bar{M}\bar{R}]} \right]_{[MX]=0},$$

by more refined techniques could be used as a test of the usefulness of this theoretical approach, for the original postulates and those implicit in equation (5) quite clearly predict that these quantities should not be zero. If in some cases this should be erroneous, the general validity of the theory will not be affected. There would have to be some modification but this would no doubt lead to a clearer understanding of the behaviour of ion exchangers.

These are the principal means by which osmotic coefficients of pure metal resins may be evaluated. They are of importance in (a) enabling the corresponding activity coefficients to be assessed, and (b) evaluating the ideal separation factors to be expected in ion exchange reactions, from which the extent of ionic interaction obtaining in the exchanger may often be assessed.

III. DETERMINATION OF THE ACTIVITY COEFFICIENT OF AN ION EXCHANGER

Hitherto the activity coefficient of a pure ion exchanger referred to the conventional standard state of pure water has been calculated in only a single case, namely that of a hydrogen-saturated exchanger (Duncan 1952). (On this basis Gregor and Gottlieb (1953) have recently calculated the activity coefficients of aqueous electrolytes absorbed by ion exchangers but not the activity coefficients of the exchanger itself.) The value of $\bar{\gamma}_H^0$ was fixed (Duncan

1952) with good accuracy from experiments on the equilibria between the exchanger and solutions of hydrochloric acid. As in the case of osmotic coefficients, numerous different experimental data may be used to fix activity coefficients. They may be broadly classified as methods depending on a knowledge of other resin activity or osmotic coefficients, those depending on a measurement of the distribution factors in an ion-exchanger reaction and those depending on the measurement of the uptake of a neutral salt by a resin with a common cation. The last-mentioned method has been discussed in detail earlier (Duncan 1952), and will not be considered further here.

(a) *Method A: From Osmotic Coefficients, assuming the Harned Rule*

Knowing the osmotic and activity coefficients of, say, a hydrogen-saturated exchanger ($\bar{\varphi}_H^0, \bar{\gamma}_H^0$) and the osmotic coefficient of the exchanger when saturated with the ion M ($\bar{\varphi}_M^0$), at the same ionic strength in the resin phase, then we have (Duncan 1952)

$$\bar{\varphi}_H^0 - \bar{\varphi}_M^0 = 1.15(\alpha_{12} - \alpha_{21})[\overline{MR}], \quad \dots\dots\dots (11)$$

and

$$\log \bar{\gamma}_H^0 / \bar{\gamma}_M^0 = (\alpha_{12} - \alpha_{21})[\overline{MR}], \quad \dots\dots\dots (12)$$

where α_{12} and α_{21} are the constants of the Harned relation

$$\log \bar{\gamma}_H = \log \bar{\gamma}_H^0 - \alpha_{12}[\overline{MR}], \quad \dots\dots\dots (13)$$

and

$$\log \bar{\gamma}_M = \log \bar{\gamma}_M^0 - \alpha_{21}[\overline{MR}], \quad \dots\dots\dots (14)$$

and $\bar{\gamma}_H$ and $\bar{\gamma}_M$ are the activity coefficients of the appropriate components in mixtures of the two species at concentrations of $[\overline{HR}]$ and $[\overline{MR}]$ at the same ionic strength. These relations will be valid only for mixtures of ions of similar type and therefore the method will not be a general one. It is justified for mixtures of hydrogen ions with the alkali metal ions, at least up to potassium, for which it has been shown that the Harned rule is often reasonably well obeyed (Glueckauf 1952). For such pairs of ions, equations (11) and (12) become

$$\bar{\varphi}_H^0 - \bar{\varphi}_M^0 = 1.15 \log \bar{\gamma}_H^0 / \bar{\gamma}_M^0. \quad \dots\dots\dots (15)$$

Hence, knowing $\bar{\varphi}_H^0$, $\bar{\varphi}_M^0$, and $\bar{\gamma}_H^0$ we may calculate $\bar{\gamma}_M^0$. The activity coefficients of the resins of lithium, sodium, and potassium shown in Figure 1 have been calculated in this way from osmotic and activity coefficients published earlier (Duncan 1952; Glueckauf 1952).

(b) *Method B: From Osmotic Coefficients using Empirical φ - γ Relations*

For ordinary aqueous solutions of electrolytes, it is found that the osmotic and activity coefficients may be represented (Glueckauf and McKay personal communication) at high concentrations by relations of the type

$$\frac{1}{Z}(\varphi - 1) = -0.15I^{\frac{1}{2}} + 1.15aI, \quad \dots\dots\dots (16)$$

and

$$\frac{1}{Z} \log_{10} \gamma = -0.261I^{\frac{1}{2}} + aI, \quad \dots\dots\dots (17)$$

where a is a common constant, I is the ionic strength, and Z is the product of the ionic charges of the cation and the anion. Eliminating a from these equations we get

$$-\frac{1}{Z}(\varphi-1) + \frac{1.15}{Z} \log_{10} \gamma = -0.15I^{\frac{1}{2}}. \quad \dots\dots\dots (18)$$

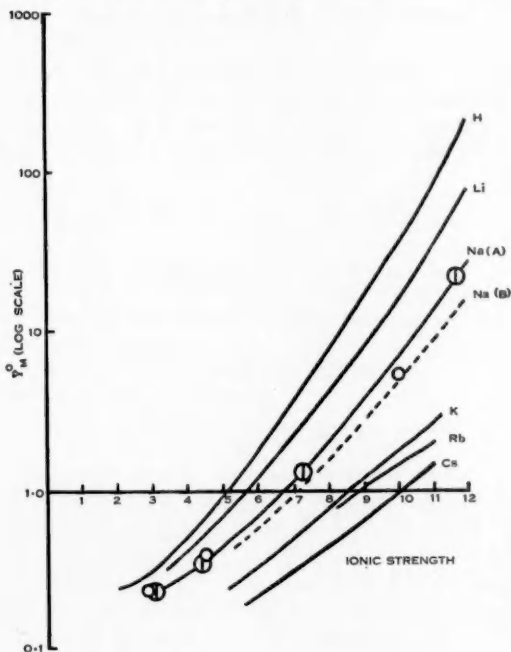


Fig. 1.—Activity coefficient curves for monovalent resins.

A (and points ⊙), γ_{Na}^0 calculated by method E.

B, γ_{Na}^0 calculated by method A.

⊙, γ_{Na}^0 calculated by method F.

The other curves were obtained as follows:

γ_{Li}^0 and γ_{K}^0 by method F.

γ_{Rb}^0 and γ_{Cs}^0 by method C.

Hence for a given value of I , a straight-line plot should be obtained between $\frac{1}{Z}(\varphi-1)$ and $\frac{1}{Z} \log \gamma$, common for all aqueous electrolytes. Such a plot is shown in Figure 2. Using only unobjectionable data, in which φ and γ have been independently determined, Glueckauf and McKay have found that equation (18)

is certainly obeyed over a wide range, except for deviations at low values, notably in the case of silver (see Fig. 2).

Now it is not possible for the coefficients relating to pure ion exchangers to follow relation (18) exactly, since the lower ends of both plots are quite different from those of normal aqueous electrolytes (Duncan 1952; Glueckauf 1952). But this merely introduces a constant term in the higher concentration ranges over which the equation may be expected to be valid, and it is found experimentally that the relation

$$\frac{1}{Z} \log \bar{\gamma}_M - \frac{A}{Z} (\bar{\varphi}_M - 1) = B \quad \dots \dots \dots (19)$$

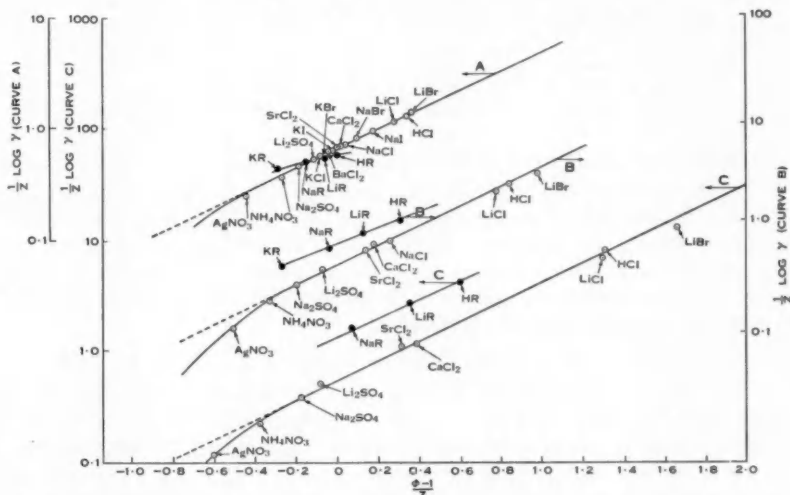


Fig. 2.—Empirical relation between osmotic and activity coefficients of aqueous electrolytes and metal resinsates.

A, $I=3$; B, $I=6$; C, $I=9$.

is obeyed for the alkali metal resinsates and an ionic strength greater than about 6. This is shown by the resinate curves of Figure 2, where it will be seen that a straight line of slightly different slope from that of aqueous electrolytes is obtained, the value of both the slope and the intercept depending on the concentration. It should be noticed that, for all the resinate data plotted here, the osmotic and activity data have been obtained independently. In the plot of Figure 2, Z was taken as 2 for univalent cations.

Once we have a relation between $\bar{\varphi}_M^0$ and $\bar{\gamma}_M^0$ such as that shown in Figure 2 for different ionic strengths it is then a simple matter to evaluate $\bar{\gamma}_M^0$ from $\bar{\varphi}_M^0$. Since some of the osmotic-activity coefficient pairs are likely to fall off the linear plot (e.g. silver resinate) one must be careful to use this method only for ions which are similar in nature to those for which the relations have been established. Quite accurate activity coefficients can then be obtained. Table 5 gives the

activity coefficients of rubidium and caesium resinsates, calculated in this way, using osmotic coefficients evaluated by method IIC above (see Table 3). Also given are the values of $\bar{\gamma}_{\text{Rb}}^0$ and $\bar{\gamma}_{\text{Cs}}^0$ obtained from the same data using method IIIA. The agreement between the two methods gives one confidence that they are sound. Not enough experimental data are yet available for divalent ions to say whether they fall on the same, or a different plot.

TABLE 5
CALCULATION OF ACTIVITY COEFFICIENTS BY AN EMPIRICAL RELATION FROM OSMOTIC
COEFFICIENTS EVALUATED BY METHOD 2B

Ion	$I = [\overline{MR}]$	$\bar{\varphi}_M$	$\bar{\gamma}_M$	$\bar{\gamma}_M$ from Same Data by Method A
Rb	8.17	0.78	0.77 ± 0.05	0.74 ± 0.02
Cs	9.24	0.65	0.82 ± 0.05	0.89 ± 0.02

(c) *Method C: From Other Activity Coefficients, assuming the Harned Rule*

In the previous two methods, the activity coefficients have been fixed *ab initio*. In this, and in the following method, it is only the changes in activity coefficient which are obtained. The absolute value must be fixed by an independent means, either by use of one of the previous methods, or by method E below. Here we assume the validity of the Harned equation, which for mixtures of univalent resinsates may be expressed as

$$\log \bar{\gamma}_H^0 / \bar{\gamma}_M^0 = (\alpha_{12} - \alpha_{21})I, \quad \dots \quad (20)$$

where α_{12} and α_{21} are constants, and I is the ionic strength. Now since $\bar{\gamma}_H^0$ is known (Duncan 1952), then $\alpha_{12} - \alpha_{21}$ may be calculated if $\bar{\gamma}_M^0$ is known at a particular value of the ionic strength. Hence $\bar{\gamma}_H^0$ may then be calculated for any ionic strength at which $\bar{\gamma}_H^0$ is known.

As with method A, this method is only reliable with pairs of ions for which the Harned rule might reasonably be expected to apply. In Figure 1 the activity coefficients of rubidium and caesium have been calculated by this method, using the previous method to fix the absolute values.

(d) *Method D: From Osmotic Curves, using the Gibbs-Duhem Relation, and knowing a Single Value of $\bar{\gamma}_M$*

This is similar to the previous method, in that a knowledge of $\bar{\gamma}_M$ at some particular ionic strength is necessary. When the Harned rule is not valid, variations in $\bar{\gamma}_M$ may be predicted from the well-known Gibbs-Duhem relationship

$$[\overline{MR}] \partial \mu_M = -55.5 \partial \mu_{\text{H}_2\text{O}}, \quad \dots \quad (21)$$

or, in a different form,

$$\partial \ln \bar{\gamma}_M = -\frac{1}{[\overline{MR}]} \partial \{[\overline{MR}](1 - \bar{\varphi}_M^0)\}. \quad \dots \quad (22)$$

Hence, provided the variation of $\bar{\varphi}_M^0$ with \overline{ME} is known, the shape of the activity coefficient curve can be predicted. Since $\bar{\gamma}_M$ is easily obtained at a particular ionic strength by methods B or E, there is no difficulty in calculating the

remainder of the activity coefficient curve from the osmotic data. This method is very much more reliable than any other in cases where the activity and osmotic

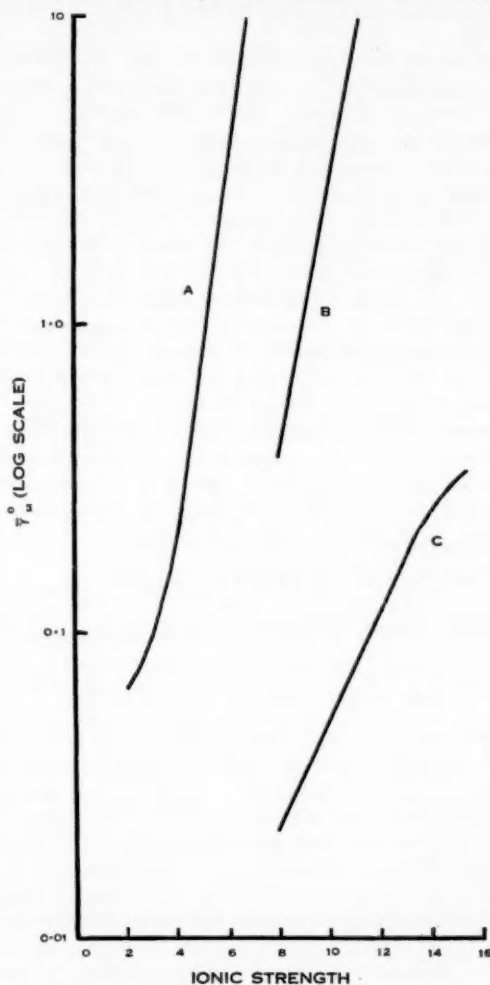


Fig. 3.—Activity coefficient plots of barium and copper resins.

A, $(\gamma_H^0)^3$.

B, γ_{Cu}^0 obtained using $\gamma_{Cu}^0 = 0.952$ at $I = 8.92$.

C, γ_{Ba}^0 obtained using $\gamma_{Ba}^0 = 0.227$ at $I = 13.7$.

coefficients do not show the normal trend, but flatten off, or show maxima at high concentrations (e.g. with multivalent resins). Figure 3 shows the

activity coefficient curves for a barium and a copper saturated exchanger, calculated in this way. The osmotic curve for barium resinate was kindly supplied by Dr. E. Glueckauf and Mr. G. B. Kitt.

(e) *Method E: From Ion Exchange Equilibria by Use of the Gibbs-Duhem Relation*

All the previously described methods have used data provided by measurements made on exchangers saturated with a single cation. There is, however, a vast amount of data available in the literature on the distribution of a pair of cations between the exchanger and a solution with a single anion. Provided the equilibrium has been determined over a sufficiently wide range of resin composition, it is then a simple matter to derive expressions relating the activity coefficients of the two metal resins in the mixed exchanger and to calculate the coefficients appropriate to the pure forms. This has been attempted before (Högfeldt, Ekedahl, and Sillén 1949; Bonner, Argersinger, and Davidson 1952), but previous authors used the pure resins as standard reference states, and omitted any variations due to changes in the external volume of the resin. Direct comparison between the activity coefficients obtained is therefore misleading since the reference state appropriate to mixed resins (viz. a pure metal resinate of the same external volume) is continually varying. Further, the calculated coefficients are hardly comparable with those of ordinary aqueous electrolytes. To indicate clearly this method of calculating the activity data the complete treatment of the thermodynamics is given below.

Consider an ion-exchange reaction of the type



for which the experimentally determined mass action product (K_c) is given by

$$\ln K_c = \ln \left\{ \frac{[\bar{B}^{n+}]^m}{[A^{m+}]^n} \times \frac{[A^{m+}]^n}{[B^{n+}]^m} \right\} = \ln \left(\frac{\bar{\gamma}_A^n}{\bar{\gamma}_B^m} \right) + \frac{P}{RT} (v_{AX_m} - v_{BX_n}), \quad \dots (24)$$

where the square brackets represent concentrations (in mole/l of swelling water), the other brackets $\{\}$ are activities, X is the common anion, and the v 's are molar volumes. The second part of this relation can easily be established by application of simple thermodynamics (Glueckauf 1952). Differentiation of equation (24) at constant temperature, assuming the molar volumes to be independent of ionic strength, leads to

$$n d(\ln \bar{\gamma}_A) - m d(\ln \bar{\gamma}_B) + \frac{v_{AX_m} - v_{BX_n}}{RT} dP - d(\ln K_c) = 0. \quad \dots (25)$$

Now for an ion exchanger with phase equilibrium between the two cations and water, we can write the Gibbs-Duhem relation in the form

$$n[\bar{A}\bar{R}] d\{\ln([\bar{A}\bar{R}]\bar{\gamma}_A)\} + m[\bar{B}\bar{R}] d\{\ln([\bar{B}\bar{R}]\bar{\gamma}_B)\} + 55.5 d(\ln \bar{a}_w) = 0, \quad \dots (26)$$

where \bar{a}_w is the water activity. Hence

$$n d[\bar{A}\bar{R}] + n[\bar{A}\bar{R}] d(\ln \bar{\gamma}_A) + m d[\bar{B}\bar{R}] + m[\bar{B}\bar{R}] d(\ln \bar{\gamma}_B) + 55.5 d(\ln \bar{a}_w) = 0, \quad \dots\dots\dots (27)$$

from which, remembering that

$$n d[\bar{AR}] = -m d[\bar{BR}], \quad \dots \dots \dots (28)$$

and substituting equation (1), we get

$$n[\bar{AR}]d(\ln \bar{\gamma}_A) + m[\bar{BR}]d(\ln \bar{\gamma}_B) + 55 \cdot 5 d \ln a_w - v_w dP / RT = 0. \quad \dots (29)$$

Multiplying equation (25) by $[\bar{AR}]$ and subtracting,

$$m([\bar{AR}] + [\bar{BR}])d(\ln \bar{\gamma}_B) + 55 \cdot 5 d \ln a_w - [v_w + [\bar{AR}](v_{AX_m} - v_{BX_n})]dP / RT \\ + [\bar{AR}]d(\ln K_c) = 0. \quad \dots \dots \dots (30)$$

Writing

$$[\bar{AR}] / ([\bar{AR}] + [\bar{BR}]) = \bar{x}_A, \quad \dots \dots \dots (31)$$

the molar fractional ratio of \bar{AR} in the exchanger, and integrating between the limits \bar{x}_A and $\bar{x}_A=1$, we get

$$m \ln (\bar{\gamma}_B / (\bar{\gamma}_B)_0) = -55 \cdot 5 \ln (a_w / (a_w)_0) + \frac{v_w}{RT} \frac{P - P_0}{[\bar{AR}] + [\bar{BR}]} \\ + \frac{v_{AX_m} - v_{BX_n}}{RT} (P \bar{x}_A - P_0) - \int_{\bar{x}_A=1}^{\bar{x}_A} \frac{v_{AX_m} - v_{BX_n}}{RT} P d\bar{x}_A \\ - \bar{x}_A \ln K_c + \ln (K_c)_0 + \int_{\bar{x}_A=1}^{\bar{x}_A} \ln K_c d\bar{x}_A, \quad \dots \dots (32)$$

where P is the swelling pressure of the exchanger in equilibrium with water, with a composition represented by \bar{x}_A ,

$(P)_0$ is the swelling pressure of a pure resinate in the AR form,

$(K_c)_0$ and $(a_w)_0$ are the values of K_c and a_w obtaining when $\bar{x}_A=1$,

and the remaining symbols have their usual significance. In this equation, the first term may usually be neglected since most ion exchange equilibria have been investigated in extremely dilute solutions where a_w is not significantly different from $(a_w)_0$. The term is most likely to be significant above about N/50 concentrations in heterovalent exchange reactions. Provided the variation of water content of the exchanger with composition is known, the results of an ion exchange equilibrium experiment may be expressed as a plot of the logarithm of the distribution coefficient, defined as in equation (24), against the molar fraction of one of the species (eqn. (31)). From such a plot it is a simple matter to evaluate the last three terms of equation (32). The remaining terms involving P are small by comparison, but may be evaluated from a knowledge of the variation of P with the external volume of the exchanger, and the variation of water content with composition. In this way we may obtain the ratio $\bar{\gamma}_B / (\bar{\gamma}_B)_0$. If $(\bar{\gamma}_B)_0$ (the activity coefficient of trace amounts of BR in a nearly pure exchanger in the AR form) can be determined by other means (see method F) then $\bar{\gamma}_B$ at any value of \bar{x}_A can be evaluated. This is of interest in two respects: first, a

knowledge of variations of activity coefficients of resins in mixtures provides information about the interaction effects which are encountered; secondly, by extrapolation of $\bar{\gamma}_B$ to $\bar{x}_B=0$ (i.e. $\bar{x}_B=1$) we obtain $\bar{\gamma}_B^0$, the activity coefficient of the pure exchanger in the *BR* form. Since this method does not utilize any data provided by osmotic experiments (except the value of P , which is of relatively little importance in equation (32)), it affords a quite independent check of activity coefficients evaluated by the methods described above.

Equation (32) allows calculation of the activity coefficient of the exchanger *BR*, which, in the conventional method of expressing the equilibrium mass product, is usually the least strongly adsorbed species. For obtaining the activity coefficient of the species *AR* an analogous equation may be obtained by integration of equation (30) between the limits \bar{x}_B and $\bar{x}_B=0$. Hence we get

$$\begin{aligned} n \ln (\bar{\gamma}_A/\bar{\gamma}_A^0) = & -55.5 \ln (a_w/a_w^0) + \frac{v_w}{RT} \frac{P-P_0}{[\bar{AR}] + [\bar{BR}]} \\ & - \frac{v_{AX} - v_{BX}}{RT} (P\bar{x}_B - P_0) + \int_{\bar{x}_B=0}^{\bar{x}_B} \frac{v_{AX} - v_{BX}}{RT} P \, d\bar{x}_B \\ & - \bar{x}_B \ln K_c - \int_{\bar{x}_B=0}^{\bar{x}_B} \ln K_c \, d\bar{x}_B, \quad \dots\dots\dots (33) \end{aligned}$$

where the zero superscripts now refer to the exchanger in the pure *AR* form. As with equation (32), relation (33) can be used for determining the value of $\bar{\gamma}_A$ in a binary mixed exchanger. But $\bar{\gamma}_A$ in the mixture is now obtained by reference to $\bar{\gamma}_A^0$, the activity coefficient of the pure exchanger, which may be determined by any of the previously described methods. A knowledge of the distribution factor for a nearly pure exchanger is not necessary. Alternatively, however, we may estimate $\bar{\gamma}_A/\bar{\gamma}_A^0$ from equation (33), determine $\bar{\gamma}_A$ from ion exchange equilibria by method *F* below, and hence obtain $\bar{\gamma}_A^0$.

This procedure for obtaining activity coefficients of the components of an ion exchange reaction would be directly applicable to the mass of experimental data available on ion exchange equilibria in the literature were some knowledge of the variations of the swelling pressure and the water content of the exchanger with composition also available. Fortunately reasonable assumptions for these factors can often be made. Thus, in the sodium-hydrogen exchanger reaction the assumption of a linear variation with composition does not introduce any serious error in the evaluated activity coefficients (Pepper and co-workers' data for the experimentally-measured water uptake of mixed sodium-hydrogen exchange resins (*loc. cit.*)). On the other hand, cases are known where this assumption would not be justified (see below).

This method has been used to calculate $\bar{\gamma}_{Na}^0$ from sodium-hydrogen ion exchange equilibria reported earlier by Reichenberg, Pepper, and McCauley (1951) and Pepper, Reichenberg, and Hale (1952) using water uptake data reported by the same authors (see Fig. 1).

(f) *Method F: From Ion Exchange Equilibria by Application of the Doynan Equation*

From equation (24) in the form

$$\ln \frac{\bar{\gamma}_A^n}{\bar{\gamma}_B^m} = \ln K_c - \frac{P}{RT}(v_{AX_m} - v_{BX_n}), \quad \dots \dots \dots (34)$$

it will be seen that, knowing the values of P and K_c appropriate to a given resin composition, the relation between the activity coefficients of the components may be simply calculated. Hence, if one of these is known the other can be determined. Equation (34) is most useful for determining the activity coefficient of a trace component in the nearly pure form of another species. With the usual reference state of a non-cross-linked exchanger at infinite dilution, we may then write, say, $\bar{\gamma}_A^n = (\bar{\gamma}_A^0)^n$, and calculate the activity coefficient ($\bar{\gamma}_B^m$) appropriate to trace amounts of the species BR in a practically pure resin in the AR form. These data are necessary for application of equations (32) and (33) to ion exchange equilibria and are therefore an essential step in the calculation of the activity coefficients of pure and mixed resins from equilibria data.

One further application of equation (34) is possible in cases where it is permissible to assume the Harned rule. In the case of univalent exchange reactions, for instance, we may write (Glueckauf 1952)

$$\frac{1}{2} \ln \left(\frac{\bar{\gamma}_A^0}{\bar{\gamma}_B^0} \right) = \ln \left(\frac{\bar{\gamma}_A}{\bar{\gamma}_B} \right) = \ln K_c - \frac{P}{RT}(v_{AX} - v_{BX}). \quad \dots \dots (35)$$

Hence, knowing the activity coefficients appropriate to one of the pure forms, that of the other may be readily calculated. In practice, this assumption is only valid for exchangers of low cross-linking, and for pairs of ions of similar type likely to form near ideal mixtures. The full circles shown in Figure 1 for $\bar{\gamma}_{Na}^0$ have been calculated in this way from equilibria data for the sodium-hydrogen exchange at the hydrogen-saturated end of the isotherm (Reichenberg, Pepper, and McCauley 1951; Pepper, Reichenberg, and Hale 1952).

IV. DISCUSSION

Figures 1 and 3 show that the shapes of the evaluated activity curves of metal resins are very similar to those obtained with aqueous electrolytes. Like activity coefficient curves of ordinary aqueous electrolytes, they sometimes obey certain mathematical relations derivable from the Harned rule. More frequently, such relations are not even approximately obeyed by activity data of either metal resins or aqueous solutions, particularly in mixtures. Such cases will be discussed in detail at another time. Here we shall merely point out where regularities are obtained in the activity coefficient curves of pure components and in relatively simple mixtures.

(a) *Relation between Activity Curves of Pure Components*

In cases where the Harned rule holds for mixtures of say copper and hydrogen ions, we may write

$$2 \log_{10} \bar{\gamma}_H^0 - \log_{10} \bar{\gamma}_{Cu}^0 = DI, \quad \dots \dots \dots (36)$$

where

$$D = \alpha_{12} - \alpha_{21}, \quad \dots \quad (37)$$

I is the ionic strength and α_{12} and α_{21} are the coefficients of the two Harned equations appropriate to the mixture. For aqueous electrolytes, relations similar to equation (36) have been found to apply tolerably well even in cases where the Harned rule is not applicable (Glueckauf, McKay, and Perring 1952). Table 6 shows the value of the constant B calculated for the pairs H/Cu and H/Ba. Equation (36) cannot be valid at very high concentrations, where the gradients of the activity coefficient curves of the bivalent resinsates tend to decrease (as they do for aqueous electrolytes), but one would expect it to be valid up to an ionic strength of 10M at least. The resinsates of the alkali metals have been excluded from Table 6 because the equation corresponding to equation (36) was explicitly or implicitly assumed in the methods of evaluating these activity coefficients.

TABLE 6
EVALUATION OF D IN EQUATION (36)

I	γ_{H}^0	γ_{Cu}^0	D	γ_{Ba}^0	D
8	8.0			0.012	0.46
9	16.2	0.91	0.27	0.024	0.44
10	36.0	1.20	0.31	0.051	0.41
11	78.0	1.45	0.33	0.082	0.45
12	202.0	1.89	0.36	0.122	0.46
13	475			0.180	0.47
14	1050			0.260	0.47

(b) *Activity Coefficients of Mixed Resinsates*

By utilizing methods III E and III F above, the activity coefficient of either of the components of a mixed ion exchanger can be calculated. If the Harned rule is applicable, then for uni-univalent exchange we might expect in equations (13) and (14) that

$$\alpha_{12} = -\alpha_{21}, \quad \dots \quad (38)$$

Table 7 gives the activity coefficients of sodium and hydrogen ions in mixed resinsates calculated from the data of Reichenberg, Pepper, and McCauley (1951) and Pepper, Reichenberg, and Hale (1952) together with the corresponding values of α_{12} and α_{21} .

It will be seen that equations (13) and (14) are often quite closely obeyed by these resinate mixtures, although even here (as with aqueous mixtures of alkali metal salts) agreement with the equations is by no means perfect and α_{12} is frequently different from $-\alpha_{21}$. Nevertheless, it is sufficiently close in many

cases (e.g. with mixtures of alkali metals) to allow one to calculate the separation factor $(K_c)_0$ for 1:1 electrolytes as

$$\ln (K_c)_0 = \frac{P}{RT}(v_{AX} - v_{BX}) + \ln \left(\frac{\bar{\gamma}_A}{\bar{\gamma}_B} \right) \quad \dots \dots \dots (39)$$

$$= \frac{P}{RT}(v_{AX} - v_{BX}) + \frac{1}{2} \ln \left(\frac{\bar{\gamma}_A^0}{\bar{\gamma}_B^0} \right), \quad \dots \dots \dots (40)$$

as has been previously pointed out by Glueckauf (1952, see equation (6.12)).

TABLE 7
VALUES OF $\bar{\gamma}_H$ AND $\bar{\gamma}_{Na}$ IN MIXED SODIUM-HYDROGEN RESINATES

	\bar{X}_{Na}	0.1	0.3	0.5	0.7	0.9
2% D.V.B.	$[\overline{NaR}]^*$	0.22	0.69	1.20	1.75	2.34
	$\bar{\gamma}_{Na}$	0.248	0.241	0.238	0.234	0.233
	$-\alpha_{21}$	0.034	0.030	0.027	0.025	0.025
	$\bar{\gamma}_H$	0.260	0.261	0.261	0.265	0.268
	α_{12}	0.014	0.014	0.015	0.011	0.011
5% D.V.B.	$[\overline{NaR}]$	0.395	1.22	2.08	2.98	3.87
	$\bar{\gamma}_{Na}$	0.364	0.351	0.343	0.346	0.350
	$-\alpha_{21}$	0.022	0.013	0.014	0.016	0.035
	$\bar{\gamma}_H$	0.482	0.486	0.489	0.458	0.416
	α_{12}	0.015	0.017	0.028	0.034	0.041
10% D.V.B.	$[\overline{NaR}]$	0.636	1.96	3.36	4.74	6.37
	$\bar{\gamma}_{Na}$	1.18	1.20	1.21	1.28	1.29
	$-\alpha_{21}$	0.022	0.0251	0.0244	0.033	0.042
	$\bar{\gamma}_H$	2.25	2.29	2.21	2.05	1.79
	α_{12}	0.038	0.040	0.046	0.050	0.056
17% D.V.B.	$[\overline{NaR}]$	0.96	3.00	5.02	7.56	10.08
	$\bar{\gamma}_{Na}$	9.68	10.78	12.50	14.50	15.70
	$-\alpha_{21}$	0.029	0.028	0.025	0.025	0.022
	$\bar{\gamma}_H$	22.9	22.7	22.5	19.1	18.8
	α_{12}	0.056	0.067	0.065	0.073	0.075

* m-equiv/ml.

V. CONCLUSIONS

The various methods of evaluating the osmotic and activity coefficients of pure metal resinates have been discussed and examples quoted. Whilst the treatment of an exchanger as a strong aqueous electrolyte clearly has limitations it is remarkable how successful this approach is in unifying the behaviour of an ion exchanger. In the case of sodium the same value of $\bar{\gamma}_{Na}^0$ is obtained from two different sets of experimental data using three independent methods of calculation. The regularities in the resin activity coefficients are closely similar to those obtained with the activity coefficients of aqueous electrolytes.

VI. SYMBOLS

In the present paper the following symbols have been used :

- a , constant,
- a_w , water activity,
- D , constant,
- K_c , mass law product allowing for the activity coefficients of the electrolytes in the aqueous solution,
- I , ionic strength.
- A, B, M, N , cations, usually associated with a common anion, X ,
- P , energy change per unit volume (has the dimensions of pressure),
- p , water vapour pressure,
- p_0 , saturation water vapour pressure at the same temperature as p is determined,
- v , molar volume,
- w , weight of water taken up by an exchanger,
- x , ionic molar fraction,
- X , ionic equivalent fraction,
- Z , product of the ionic charges of the cation and anion,
- α_{12} and α_{21} are coefficients of the Harned type relations, for example,

$$\ln (\gamma_M) = \ln (\gamma_M^0) + \alpha_{12}[NR], \text{ and}$$

$$\ln \gamma_N = \ln (\gamma_N^0) + \alpha_{21}[MR],$$

γ , mean molal ionic activity coefficient,

ϕ , mean molal ionic osmotic coefficient,

μ , chemical potential,

$\{\}$ thermodynamic activity,

$[\]$ molal concentration (mole/1000 g water).

A bar (as in $\bar{\gamma}_H$) denotes that the quantity refers to the exchanger phase.

No difference mark (as in γ_H) denotes that the quantity refers to the external solution.

Suffix j (as in \bar{a}_j) refers to the component j .

Superscript 0 (as in γ^0) refers to a solution of the pure electrolyte (or resinate) at the same ionic strength as the mixture.

VII. ACKNOWLEDGMENTS

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THEORY OF ALTERNATING CURRENT POLAROGRAPHY

II. SIGNIFICANCE OF THE HEYROVSKÝ-ILKOVIČ EQUATION AND ITS RELATION TO THE PRODUCTION OF A.C. POLAROGRAPHIC WAVES

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Summary

The significance of the Heyrovský-Ilkovič equation is discussed and the relationship between reversibility of the electrochemical reaction and polarographic reversibility critically examined. It is shown that even reversible electrochemical processes might yield D.C. polarograms of the irreversible type. The relationship between different types of electrode reactions and the production of A.C. polarographic waves is elucidated.

I. INTRODUCTION

In numerous previous publications (Breyer and Gutmann 1946a, 1946b, 1947a, 1947b; Breyer and Hacobian 1952a, 1952b, 1954; Delahay and Adams 1952) the theoretical foundations of polarographic processes employing the superposition of a small sinusoidal alternating voltage upon the direct potential applied to the dropping mercury electrode were discussed. As has been shown in Part I of this series, the applied direct potential is responsible for the electrode process whereas the superposed alternating field produces periodic concentration changes near the electrode. These concentration changes result in an alternating current whose magnitude depends on the applied direct potential. The graphs obtained by plotting the value of the alternating current against the direct potential have been termed "A.C. waves". It is the object of the present paper to elucidate the relationship between the D.C. electrode process and the alternating current obtained.

The production of A.C. polarographic waves is intimately connected with the reversibility of the underlying electrode reaction. It will be necessary, therefore, to discuss first of all the conditions under which a reversible D.C. polarogram is obtained.

II. DEFINITIONS AND NOTATION

The following definitions and notation are used in the present paper:

Electrochemical reaction: reaction including electron transfer as well as inherent processes accompanying it, such as solvation/desolvation, amalgamation/deamalgamation, etc.

Secondary reaction: reaction at the electrode not involving electron transfer, such as dimerization, protonization, etc.

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Electrode reaction : overall reaction including both electrochemical and secondary reactions.

Tensammetric process : adsorption/desorption process resulting in an A.C. wave and due to oscillatory movement of dipoles at the electrode/solution interface (cf. Breyer and Hacopian 1952c).

A_0, B_0 , species at the electrode undergoing an electrochemical reaction,

A_1, B_1 , corresponding species in the adsorbed state,

A, B , corresponding species in the bulk of the solution,

c_i , bulk concentration of reactant,

D_i , diffusion coefficient of species i ,

E, E_d , applied direct potential and the polarographic half-step potential respectively,

E_s, E_n , summit potential of the A.C. polarographic wave and of the tensammetric wave respectively,

F , Faraday,

i, i_d , direct polarographic current and diffusion current respectively,

$\Delta i(E_s)$, alternating polarographic current at the summit potential,

k , specific rate of the change occurring; the subscript indicates the nature of the change. Examples $k_{A_0B_0}$ = specific rate of the electrochemical reaction $A_0 \rightarrow B_0$; $k_{B_0A_0}$ = rate of the reverse reaction; $k_{A_0P_0}$ = specific rate of secondary reaction $A_0 \rightarrow P_0$; $k_{A_0A_1}$ = specific rate of the adsorption process $A_0 \rightarrow A_1$. Electrochemical rates generically are denoted by k_e , those of secondary reactions by k_s , and those of tensammetric processes by k_t ,

n , number of electrons involved in the electrochemical reaction,

P_0, Q_0 , species at the electrode resulting from secondary reactions of A_0, B_0 ,

P_1, Q_1 , corresponding species in the adsorbed state,

P, Q , corresponding species in the bulk of the solution,

P_{01}, P_{D1} , orientation and distortion polarizations of surface active dipoles at the electrode interface,

r_i , diffusion rate operator of species i having dimensions LT^{-1} , e.g. $r_A [\equiv D_A(\partial/\partial x)]$ refers to the diffusion rate of species A from the bulk of the solution to the electrode,

S , area of electrode surface at maximum age of the mercury drop,

T , absolute temperature,

ΔV_0 , amplitude of alternating voltage,

ω , angular frequency of the alternating current.

III. TYPE OF ELECTRODE PROCESS AND D.C. POLAROGRAPHIC REVERSIBILITY

The polarographic process is a complex one. It consists of a number of part processes. Those always present are :

- (i) Diffusion of reactant from the bulk of the solution to the electrode surface.

- (ii) Electrochemical reaction.
- (iii) Diffusion of resultant from the electrode into the bulk of the solution.*

Part processes which might be either present or absent, depending on the particular polarographic process, are :

- (iv) Secondary reactions, most commonly reactions between resultant molecules (e.g. dimerization), between resultant molecules and other constituents present (e.g. protonization), etc.
- (v) Adsorption/desorption processes : The reason for assigning to these a special group is that they are of major importance in A.C. electrode reactions.

Discussion in papers preceding this has shown that the reversibility or otherwise of the D.C. polarographic process is of fundamental importance for theoretical considerations of the A.C. polarographic process. It is obvious how a thermodynamically irreversible electrochemical reaction will result also in an irreversible polarographic process. On the other hand, as is shown in the following, even reversible electrochemical reactions might, under certain conditions, yield polarograms of the irreversible type (cf. also Zimmerman and Gropp 1950), that is, polarograms which do not obey the Heyrovský-Ilkovič (1935) equation

$$E = E_1 + (RT/nF) \ln (i_d - i)/i.$$

It will be necessary at this point to consider the contemplated electrode system.

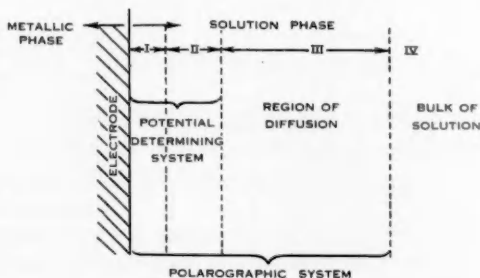


Fig. 1.—Diagrammatic representation of the electrode-solution system.

The potential determining system comprises regions I and II (Fig. 1), that is, that space within which the electrode reaction occurs. It is assumed that unadsorbed particles can occupy both regions, whereas the adsorbed species is found only in region I. The polarographic system consists of the potential determining one and of the surrounding diffusion region (region III). These

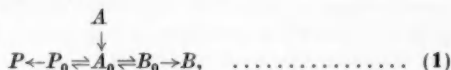
* It is to be noted that under polarographic conditions the bulk concentration of reactant can be assumed to remain constant, whereas the bulk concentration of resultant is practically equal to zero.

systems may also extend into the electrode surface depending on whether or not the resultant can diffuse into the electrode metal.

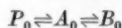
The relationship between the reversibility of the electrochemical reaction and polarographic reversibility can now be discussed.

(a) *Electrode Processes not involving Adsorption*

Consider the reaction sequence (1)



symbolizing a reversible electrochemical reaction and a reversible secondary reaction. It is assumed throughout that diffusion is the slowest process. Now, more or less perfect thermodynamic reversibility depends on how far the contemplated system can be isolated. Hence, ideal reversibility will be more nearly attained when the relevant process is reversible and fast compared with the rates of the secondary reactions. Applied to the present case that means that the electrode reaction



is reversible since preceding and following diffusion processes are slow.

For stationary concentrations of P_0 , $\partial[P_0]/\partial t = 0$,

$$r_P\{[P_0] - [P]\} + k_{P_0A_0}[P_0] - k_{A_0P_0}[A_0] = 0. \quad \dots \quad (6)$$

Similarly at equilibrium

$$\partial[A_0]/\partial t = \partial[B_0]/\partial t = 0,$$

that is

$$k_{A_0B_0}[A_0] + k_{A_0P_0}[A_0] - k_{B_0A_0}[B_0] - k_{P_0A_0}[P_0] - r_A\{[A] - [A_0]\} = 0, \quad \dots \quad (7)$$

and

$$-k_{A_0B_0}[A_0] + k_{B_0A_0}[B_0] + r_B\{[B_0] - [B]\} = 0. \quad \dots \quad (8)$$

The polarographic diffusion current is expressed as

$$i_d = nFSr_A[A], \quad \dots \quad (9)$$

and

$$i = nFS\{k_{A_0B_0}[A_0] - k_{B_0A_0}[B_0]\}. \quad \dots \quad (10)$$

Combining (6), (7), (8), (9), and (10) and remembering that the bulk concentrations of B and P equal zero

$$(i_d - i)/i = (r_A[A_0] + r_P[P_0])/r_B[B_0]. \quad \dots \quad (11)$$

When $r_P[P_0] \rightarrow 0$, that is, when the equilibrium, $P_0 \rightleftharpoons A_0$, is shifted very much to the right,

$$(i_d - i)/i = [A_0]/[B_0],$$

when $r_A = r_B$; that is, the Heyrovský-Ilkovič equation applies. In other words, under these conditions the reversible electrochemical reaction yields also a polarogram of the reversible type. It is proposed to call this type of reaction

"polarographically reversible". If, on the other hand $[P_0]$ is finite, only part of the polarographic current is diffusion controlled; another part is due to the kinetics of the secondary reaction. Although the underlying electrode reaction is reversible, the Heyrovský-Ilkovič equation is not obeyed and the process is "polarographically irreversible". It can be, therefore, concluded that a reaction is polarographically reversible only then, when secondary reactions are absent.

Summarizing: Reversible electrode reactions can give rise to either reversible or irreversible polarographic processes, depending on (i) whether the speed of the electrochemical reaction is greater or less than the rate of diffusion of the electroactive forms, and (ii) whether or not secondary reactions are involved.

The resulting types of electrode processes are presented in Table 1.

TABLE 1
TYPES OF ELECTRODE PROCESSES AND THEIR RELATION TO POLAROGRAPHIC REVERSIBILITY

Type of Process	Secondary Reactions	Relative Magnitudes of k_e , k_s , and r	Electrochemical Reaction	Type of Polarogram
1	Absent	$k_e \gg r$	Reversible	Reversible
2	Absent	$k_e \sim r$	Reversible	Irreversible
3	Present and irreversible	$k_e \gg k_s$	Reversible	Irreversible
4	Present and reversible	Any	Reversible	Irreversible
5	Present or absent	Any	Irreversible	Irreversible

Type 1 represents the ideally reversible D.C. polarographic case. Irreversible D.C. polarographic processes of type 2 have received much attention by different workers (e.g. Eyring, Marker, and Kwoh 1949; Tanaka and Tamamushi 1949, 1951; Saito 1950; Goto and Tachi 1951; Delahay 1951, 1953; Koutecky 1951; Kern 1954). Processes of type 4 are those where D.C. polarographic irreversibility is due to secondary reactions. This type of electrode reaction has been discussed by Kivalo (1953). Despite an electrochemical reaction faster than diffusion, irreversible log plots are obtained, due to the fact that the resultant is involved in a secondary reaction.

(b) *Electrode Processes involving Adsorption*

Consider the sequence (2):



At equilibrium

$$\partial[A_0]/\partial t = \partial[A_1]/\partial t = \partial[B_0]/\partial t = 0,$$

that is,

$$r_A\{[A] - [\bar{A}_0]\} + k_{A_1A_0}[A_1] - k_{A_1A_1}[A_0] = 0, \quad \dots (12)$$

$$k_{A_1A_1}[A_0] + k_{B_1A_1}[B_0] - k_{A_1A_0}[A_1] - k_{A_1B_0}[A_1] = 0, \quad \dots (13)$$

and

$$r_B\{[B_0] - [B]\} + k_{B_1A_1}[B_0] - k_{A_1B_0}[A_1] = 0. \quad \dots (14)$$

Also, since diffusion is the rate determining step,

$$i_d/(nFS) = r_A[A], \quad \dots (15)$$

and

$$i/(nFS) = k_{A_1B_0}[A_1] - k_{B_1A_1}[B_0]. \quad \dots (16)$$

Combining (12), (13), (14), (15), and (16), remembering that $[B] = 0$, and assuming $r_A = r_B$

$$(i_d - i)/i = [A_0]/[B_0]. \quad \dots (17)$$

Hence, the Heyrovský-Ilkovič equation is valid, provided the concentrations of the electroactive forms are small, compared with the available electrode area. Only when this condition is satisfied, the velocity of the process $A_0 \rightarrow A_1$ can be expressed as $k_{A_1A_0}[A_0]$ and equations (12), (13), and (14) apply.

Neglecting secondary reactions, three types of reaction sequences can now be distinguished.

- (2): as shown above, where the reactant is adsorbed prior to electrochemical reaction.
- (3): $A \rightarrow A_0 \rightleftharpoons B_1 \rightleftharpoons B_0 \rightarrow B$, here the resultant is adsorbed.
- (4): $A \rightarrow A_0 \rightleftharpoons A_1 \rightleftharpoons B_1 \rightleftharpoons B_0 \rightarrow B$, here the electrochemical reaction involves both reactant and resultant in the adsorbed state.

When the fraction of the electrode surface covered with adsorbed species is small, sequences (2), (3), and (4) should yield reversible D.C. polarograms. Irreversible character can develop as a result of (i) intrinsic irreversibility of the electrochemical reaction, (ii) the presence of secondary reactions, or (iii) large coverage of the electrode surface due either to high adsorbability or to relatively large bulk concentration of electroactive substance.

IV. ELECTRODE PROCESSES IN THE PRESENCE OF ALTERNATING FIELDS

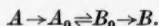
When a small sinusoidal alternating voltage is superposed on the direct potential applied to a dropping mercury electrode, various types of A.C. waves are produced depending on the nature of the electrode reaction. The alternating current is due to changes in the complex permittivity ($\partial\chi/\partial E$) of the "active space" in virtue of one of the following electrode processes:

(a) Thermodynamically Reversible Electrochemical Reactions not involving Adsorption

This type of process is most commonly encountered in the reversible reduction of inorganic ions.

Since the criterion for production of an A.C. wave is the reversibility of the electrochemical reaction, processes of type 1 to 4 (Table 1) will result in A.C. waves, despite the fact that types (2), (3), and (4) are polarographically irreversible.

The simplest process involving a reversible electrochemical reaction may be represented by sequence (5):



In such a process, an A.C. wave is obtained when the frequency of the alternating voltage is smaller than the rate of the electrochemical reaction. With increasing frequency the alternating current at first increases, to decrease progressively as the electrochemical reaction lags more and more behind the field changes. This incidentally is true of all A.C. polarographic processes whatever the underlying electrode reaction.

The alternating current at E_e , is given by the general expression:

$$\Delta i_{(E_e)} = gf(\omega, k_e, D), \quad \dots \dots \dots (18)$$

where

$$g = g(n, F, S, R, T, \Delta V_0, c_B), \quad \dots \dots \dots (19)$$

and when $\omega \ll k_e$

$$\Delta i_{(E_e)} = gf(\omega, D)^* \quad \dots \dots \dots (20)$$

(b) *Thermodynamically Reversible Adsorption/Desorption Processes*

This type of process gives rise to a tensammetric wave (Breyer and Hacobian 1952c) and can be represented by



Here the magnitude of the resulting alternating current depends, *inter alia*, on the tensammetric rate constant and on the orientation and distortion polarizations of the dipoles at the electrode/solution interface† so that

$$\Delta i_{(E_e)} = g' \cdot f(\omega, k_D, D), \quad \dots \dots \dots (21)$$

where

$$g' = g'(S, R, T, \Delta V_0, c_B, P_{Di}, P_{Oi}). \quad \dots \dots \dots (22)$$

Electron transfer is absent and hence no faradaic current flows. The alternating current is due solely to the oscillatory movement of dipoles at the electrode. It is noteworthy that tensammetric processes generally follow the field changes to higher frequencies than most of the processes in Section III (a).

(c) *Reversible Electrochemical Reactions involving Rearrangement and/or Adsorption*

This type of process (reaction sequences (2), (3), and (4)) is common in polarography of organic compounds. The magnitude of the resulting alternating current depends on a number of additional parameters. The organic molecules

* The explicit form of eqn. (20) has been given in Part I (eqn. (40)); the explicit form of eqn. (18) is the subject of Part III of this series (Breyer, Bauer, and Hacobian, 1955).

† It should be kept in mind that in virtue of the non-uniform field at the electrode-solution interface, dipole character might be imparted also to symmetrical molecules not showing a dipole moment when in the bulk of the solution.

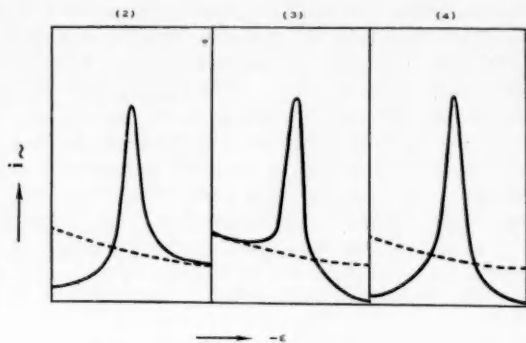


Fig. 2.—Schematic A.C. polarograms.

— Corresponding to reaction sequences (2), (3), and (4).
 Base current (supporting electrolyte).

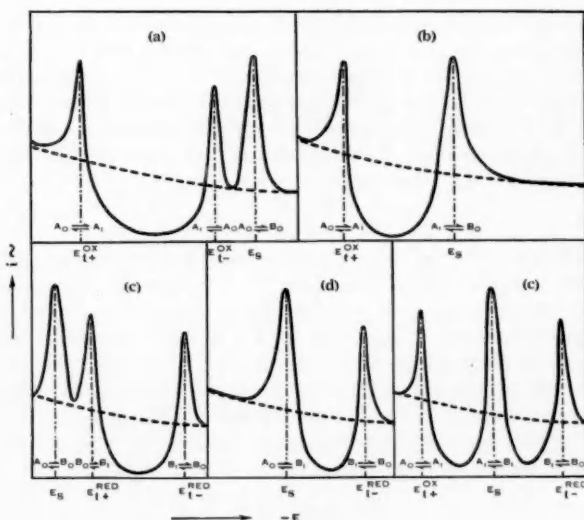


Fig. 3.—Schematic A.C. polarographic and tensammetric waves. E_{t+}^{Ox} , E_{t-}^{Ox} , E_{t+}^{Red} , E_{t-}^{Red} , positive and negative tensammetric summit potentials of the oxidized and reduced forms respectively.

E_s , A.C. polarographic summit potential.

— A.C. polarograms.

.... Base current (supporting electrolyte).

(a) and (b): only the oxidized form is adsorbable.

(c) and (d): only the reduced form is adsorbable.

(e) both forms are adsorbable.

undergoing electrochemical reaction are generally polar and adsorbed at the electrode. The alternating field will produce periodic rearrangement of *both* reactant and resultant molecules (in contradistinction to tensammetry where only one molecular species is involved). It is obvious how the rearrangement must bring about a very pronounced change in the permittivity of the active space since the dipole characteristics of reactant and resultant molecules differ greatly. Hence the alternating current produced in this type of process ("rearrangement current"; Breyer 1953) is as a rule greater than that for a process involving an equivalent number of inorganic ions. The different parameters involved in this type of A.C. process can be represented by

$$\Delta i_{(re)} = g'' \cdot f(\omega, k_s, k_e, k_i, D), \quad \dots \dots \dots (23)$$

where

$$g'' = g''(n, F, S, R, T, \Delta V_0, c_B, P_{D1}, P_{O1}). \quad \dots \dots \dots (24)$$

Adsorption processes are recognized from the lowering of the base current before and/or after the polarographic wave (Breyer and Hacobian 1952c; Doss and Kalyanasundaram 1952). Hence the different electrode reactions will result in differently shaped A.C. waves as shown in Figure 2.

Both tensammetric and polarographic waves might be encountered in one and the same polarogram. According to the relative values of the polarographic and tensammetric peak potentials, a number of possible polarograms can be envisaged (Fig. 3). A polarogram as that shown in Figure 3 (d) has been encountered in the A.C. polarography of *perinaphthenone* in acid or neutral solutions. A polarogram as that represented schematically by Figure 3 (e) is obtained with *perinaphthenone* in alkaline solutions.

V. CONCLUSION

The theoretical discussion in the preceding sections covers only a small fraction of the possible types of processes. It represents an attempt at elucidation of the mechanisms involved in the production of the more common types of A.C. polarographic waves. It should be borne in mind that before any specific conclusion can be drawn regarding a particular A.C. polarogram, an *a priori* knowledge of the underlying electrode process is a prerequisite. The majority of the electrode reactions discussed seems not yet amenable to quantitative treatment. A few, however, can be treated quantitatively as will be shown in the succeeding papers of this series.

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THEORY OF ALTERNATING CURRENT POLAROGRAPHY

III. FREQUENCY OF ALTERNATING FIELD AND REACTION RATE

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Summary

The equation of the A.C. polarographic current for processes where the frequency of the alternating field is comparable with the rate of the electrode reaction is derived. Relative values of equilibrium rate constants of some first order electrode reactions are evaluated experimentally.

I. INTRODUCTION

It is the object of the present paper to extend the theory of A.C. polarography as presented in Part I of this series (Breyer and Hacobian 1954) to cover the special case when the frequency of the superposed alternating voltage is comparable with the rate of the electrochemical reaction; the latter is assumed to proceed reversibly. In this case, reaction equilibrium no longer follows the field changes and the alternating current is less than that predicted by equation (40) of Part I of this series, where it was assumed that the rate of the reversible electrochemical reaction is far greater than the frequency of the alternating voltage.

Here it will be shown how equation (40) (loc. cit.) can be modified to apply to the present case.

II. NOTATION

The following notation is used in the present paper :

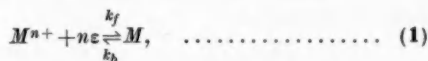
- A , surface area of the electrode at maximum age of mercury drop,
- $c_{(0,\tau,E_s)}^{\text{ox}}$, $c_{(0,\tau,E_s)}^{\text{red}}$, instantaneous concentration of oxidized and reduced particles at the electrode surface and at the potential E_s ,
- c_b , bulk concentration of electroactive form,
- $\Delta c_{(0,\tau,E_s)}$, concentration change at the electrode surface,
- $\Delta c_{0(0,E_s)}$ or Δc_0 , amplitude of concentration change at the electrode surface,
- D , diffusion coefficient of electroactive forms,
- E_s , summit potential of A.C. polarographic wave,
- F , Faraday,
- $i_{(E_s)}$, direct current at E_s ,
- $i_{t(E_s)}$, total instantaneous current,

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- $\Delta i(E_s)$, alternating current at E_s ,
 $\Delta i_0(E_s)$, amplitude of alternating current at E_s ,
 k_s , equilibrium specific rate constant at E_s having dimensions LT^{-1} ,
 k_f, k_b , forward and backward specific rate constants of the reaction $M^{n+} + n\varepsilon \rightleftharpoons M$ in absence of applied potential,
 M^{n+}, M , oxidized and reduced species at the electrode surface,
 n , number of electrons transferred,
 R , molar gas constant,
 T , absolute temperature,
 $\Delta V, \Delta V_0$, instantaneous superposed alternating voltage and amplitude respectively,
 α , fraction of the applied potential which facilitates the forward electrochemical process (Glasstone, Laidler, and Eyring 1941),
 $1-\alpha$, fraction of the applied potential which retards the backward process (Glasstone, Laidler, and Eyring 1941).
 θ , phase angle between alternating current and voltage,
 θ' , phase angle between concentration change and alternating voltage,
 ω , frequency of alternating voltage.

III. THEORETICAL

Consider the reversible first-order electrochemical reaction



supposed to occur at the half-step potential $E_{\frac{1}{2}}$ which is also identical with the summit potential E_s . A small sinusoidal alternating voltage

$$\Delta V = \Delta V_0 \cos \omega\tau, \quad \dots \quad (2)$$

is superposed.

The instantaneous concentration of reducible particles, $c_{(0,\tau,E_s)}^{Ox}$, at the electrode surface is given by

$$c_{(0,\tau,E_s)}^{Ox} = c_{(0,E_s)}^{Ox} + \Delta c_{(0,\tau,E_s)}, \quad \dots \quad (3)$$

and

$$\Delta c_{(0,\tau,E_s)} = \Delta c_{(0,E_s)} \cos(\omega\tau + \theta'). \quad \dots \quad (4)$$

At E_s

$$c_{(0,E_s)}^{Ox} = \frac{1}{2}c_B, \quad \dots \quad (5)$$

and hence

$$c_{(0,\tau,E_s)}^{Ox} = \frac{1}{2}c_B + \Delta c_{(0,\tau,E_s)}. \quad \dots \quad (6)$$

Similarly

$$c_{(0,\tau,E_s)}^{red} = \frac{1}{2}c_B - \Delta c_{(0,\tau,E_s)}. \quad \dots \quad (7)$$

The total current flowing through the cell can be expressed (after Glasstone, Laidler, and Eyring 1941) by :

$$i_{t(E_s)} = nFA [k_f \cdot c_{(0,\tau,E_s)}^{\text{ox}} \cdot e^{-(\alpha nF\varepsilon)/RT} - k_b \cdot c_{(0,\tau,E_s)}^{\text{red}} \cdot e^{(1-\alpha)nF\varepsilon/RT}], \quad \dots (8)$$

where ε is the total applied instantaneous voltage, that is,

$$\varepsilon = E_s + \Delta V_0 \cos \omega\tau. \quad \dots (9)$$

The total instantaneous current is the sum of the direct and alternating current, that is,

$$i_{t(E_s)} = i_{(E_s)} + \Delta i_{(E_s)}. \quad \dots (10)$$

Now

$$\Delta i_{(E_s)} = nFA \cdot \Delta c_{0(0,E_s)} \sqrt{\omega D} \cdot \cos(\omega\tau + \theta' + \pi/4), \quad \dots (11)$$

(Breyer and Hacobian 1954) and the amplitude of the alternating current

$$\Delta i_{0(E_s)} = nFA \Delta c_{0(0,E_s)} \sqrt{(\omega D)}. \quad \dots (12)$$

Expanding (11) we obtain :

$$\begin{aligned} \Delta i_{(E_s)} &= nFA \Delta c_0 \sqrt{(\omega D/2)} \cdot (\cos \theta' - \sin \theta') \cdot \cos \omega\tau \\ &\quad - nFA \Delta c_0 \sqrt{(\omega D/2)} \cdot (\cos \theta' + \sin \theta') \cdot \sin \omega\tau. \quad \dots (13) \end{aligned}$$

Equating

$$k'_f = k_f \cdot e^{-(\alpha nF E_s)/RT}, \quad \dots (14)$$

and

$$k'_b = k_b \cdot e^{[(1-\alpha)nF E_s]/RT}, \quad \dots (15)$$

equation (8) reduces to

$$\begin{aligned} i_{t(E_s)} &= nFA [k'_f (\frac{1}{2}c_B + \Delta c_{(0,\tau,E_s)}) \cdot e^{-(\alpha nF \Delta V_0 \cos \omega\tau)/RT} \\ &\quad - k'_b (\frac{1}{2}c_B - \Delta c_{(0,\tau,E_s)}) \cdot e^{[(1-\alpha)nF \Delta V_0 \cos \omega\tau]/RT}]. \quad \dots (16) \end{aligned}$$

Since ΔV_0 is small, $nF \Delta V_0 \cos \omega\tau/RT$ is also small, and we can write to a first approximation :

$$e^{nF \Delta V_0 \cos \omega\tau/RT} = 1 + (nF \Delta V_0 \cos \omega\tau)/RT. \quad \dots (17)$$

The direct current is given by

$$i_{(E_s)} = nFA (k'_f \cdot \frac{1}{2}c_B - k'_b \cdot \frac{1}{2}c_B). \quad \dots (18)$$

Substituting (10), (17), and (18) into (16) and remembering that α equals 0.5 at E_s , we obtain

$$\begin{aligned} \Delta i_{(E_s)} &= nFA \{k'_f [\Delta c_0 \cdot \cos(\omega\tau + \theta') - (c_B nF \Delta V_0 \cos \omega\tau)/4RT] \\ &\quad + k'_b [\Delta c_0 \cos(\omega\tau + \theta') - (c_B nF \Delta V_0 \cos \omega\tau)/4RT]\}. \quad \dots (19) \end{aligned}$$

At E_s , the rate constants k'_b , k'_f , and k_e are approximately equal and hence

$$\begin{aligned} \Delta i_{(E_s)} &= [2nFA k_e \Delta c_0 \cos \theta' - (n^2 F^2 A \Delta V_0 k_e c_B)/2RT] \cdot \cos \omega\tau \\ &\quad - (2nFA k_e \Delta c_0 \sin \theta') \cdot \sin \omega\tau. \quad \dots (20) \end{aligned}$$

Comparing equations (13) and (20) and equating coefficients of $\sin \omega \tau$ and $\cos \omega \tau$, we obtain

$$\cot \theta' = 2kz - 1, \quad \dots \dots \dots (21)$$

where

$$z = \sqrt{(2/\omega D)}. \quad \dots \dots \dots (22)$$

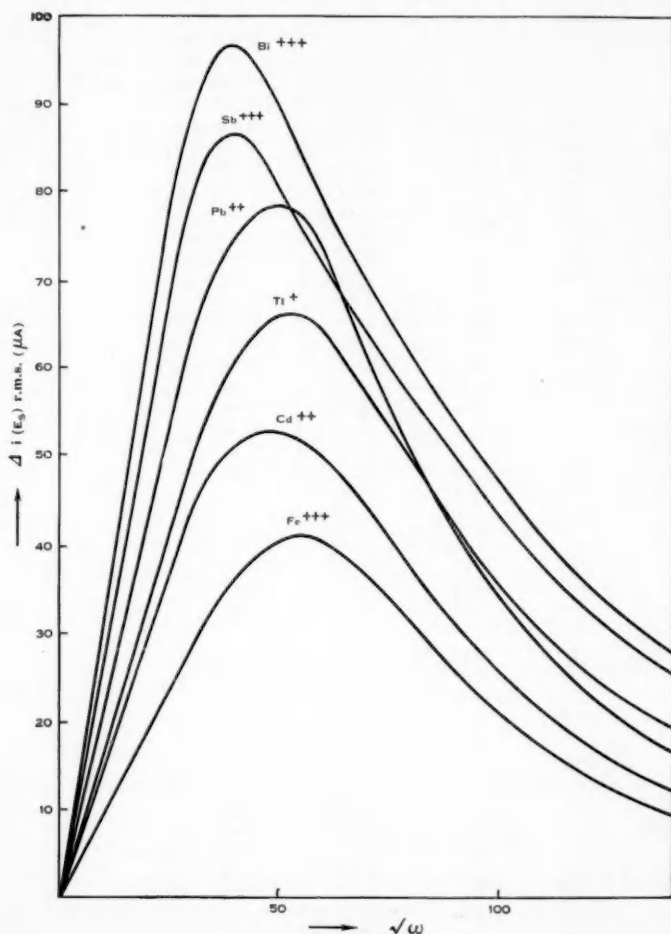


Fig. 1.— $\Delta i(E_p)_{\text{r.m.s.}}/\sqrt{\omega}$ curves corresponding to the reduction of 10^{-3}N Bi^{+++} , Sb^{+++} , Pb^{++} , Cd^{++} , Tl^{+} in 0.5N HCl , and 10^{-3}N Fe^{+++} in $0.1\text{M ammonium oxalate}$. The figure represents curves of best fit obtained from experimental data as shown in Table 1. A.C. 15 mV r.m.s. ; $T, 20^\circ\text{C}$.

TABLE 1

OBSERVED AND CALCULATED $\Delta i(E_p)_{r.m.s.}$ VALUES

$T, 20^\circ \text{C}$; A.C. 15 mV r.m.s.; area of electrode at max. age of mercury drop (zero applied e.m.f.): $2.1 \times 10^{-2} \text{ cm}^2$; cell impedance: 110 complex ohms

Solution	Frequency (c/s)	$\Delta i(E_p)_{r.m.s.}$	(μA)	Obs. Calc.	Mean	Max. Deviation from Mean (%)
		Calc.	Obs.			
10 ⁻³ N Tl ⁺ in 0.5N HCl	55	32.8	30.9	0.93	0.88	8.2
	110	48.1	44.4	0.92		
	140	54.0	46.9	0.87		
	220	61.5	53.6	0.87		
	320	72.2	64.7	0.90		
	500	74.5	66.1	0.89		
	750	73.5	59.2	0.81		
	1000	71.5	51.3	0.71		
	2000	65.5	30.0	0.46		
	5000	61.5	19.2	0.31		
10 ⁻³ N Fe ⁺⁺⁺ in 0.1N ammonium oxalate	55	23.0	18.1	0.79	0.74	6.7
	110	34.5	24.4	0.72		
	140	39.0	28.2	0.72		
	220	43.5	34.3	0.79		
	320	50.0	36.7	0.73		
	500	52.4	41.2	0.79		
	750	52.2	38.5	0.74		
	1000	50.5	31.4	0.62		
	2000	47.1	17.3	0.37		
	5000	43.5	9.1	0.21		
10 ⁻³ N Cd ⁺⁺ in 0.5N HCl	55	33.3	28	0.84	0.82	8.5
	110	46.2	39.9	0.86		
	140	51.3	43.0	0.83		
	220	57.5	48.6	0.85		
	320	65.0	51.2	0.79		
	500	68.0	51.5	0.75		
	750	66.9	46.0	0.70		
	1000	66.0	37.0	0.57		
	2000	65.8	20.6	0.31		
	5000	65.2	12.2	0.19		
10 ⁻³ N Pb ⁺⁺ in 0.5N HCl	55	47.5	41.0	0.86	0.81	6.1
	110	71.4	57.2	0.80		
	140	77.6	65.2	0.84		
	220	88.6	69.3	0.78		
	320	97.5	77.5	0.80		
	500	98.0	77.9	0.79		
	750	97.5	63.8	0.65		
	1000	94.1	51.5	0.55		
	2000	87.3	28.1	0.32		
	5000	80.7	14.5	0.15		

TABLE 1 (Continued)

Solution	Frequency (c/s)	$\Delta i(E_s)_{r.m.s.}$	\cdot (μA)	Obs. Calc.	Mean	Max. Deviation from Mean (%)
		Calc.	Obs.			
10 ⁻² N Sb ⁺⁺⁺ in 0.5N HCl	55	73.5	48.0	0.65	0.71	8.5
	110	104.0	72.2	0.69		
	140	110.0	79.1	0.72		
	220	112.5	86.4	0.76		
	320	118.6	86.4	0.73		
	500	117.0	77.0	0.66		
	750	114.0	66.2	0.58		
	1000	107.0	60.0	0.56		
	2000	103.0	39.6	0.38		
	5000	96.5	17.4	0.16		
10 ⁻² N Bi ⁺⁺⁺ in 0.5N HCl	55	73.5	56.0	0.76	0.80	6.2
	110	104.0	82.1	0.79		
	140	110.0	88.0	0.80		
	220	112.5	96.3	0.85		
	320	118.6	96.5	0.81		
	500	117.0	80.0	0.68		
	750	114.0	76.4	0.67		
	1000	107.0	62.2	0.58		
	2000	103.0	43.0	0.42		
	5000	96.5	18.1	0.19		

Similarly

$$\Delta c_0 = \frac{c_B n F \Delta V_0}{2RT(4 - 4/k_e z + 2/k_e z^2)^{\frac{1}{2}}}, \quad \dots \dots \dots (23)$$

when $k_e \gg \omega D$, (23) reduces to

$$\Delta c_0 = \frac{c_B n F \Delta V_0}{2RT}, \quad \dots \dots \dots (24)$$

which is identical with equation (36) of Part I (Breyer and Hacobian 1954) for small ΔV_0 . The r.m.s. alternating current is given by

$$\Delta i(E_s)_{r.m.s.} = \frac{nFA\Delta c_0 \sqrt{\omega D}}{\sqrt{2}}. \quad \dots \dots \dots (25)$$

(Breyer and Hacobian 1954) and substituting (22) and (23) into (25) we obtain

$$\Delta i(E_s)_{r.m.s.} = \frac{n^2 F^2 A \Delta V_0 c_B}{4\sqrt{2}RT[1/(\omega D) - 1/(2k_e^2 \omega D)^{\frac{1}{2}} + 1/(4k_e^2)]^{\frac{1}{2}}}. \quad \dots \dots \dots (26)$$

To find the frequency ($\omega_{max.}$) at which the alternating current becomes a maximum, we set $\partial(\Delta i)/\partial \omega = 0$, and thus obtain

$$k_e = \sqrt{(\omega_{max.} D/8)}. \quad \dots \dots \dots (27)$$

After obtaining $\omega_{max.}$ graphically by plotting Δi versus ω (or more conveniently $\sqrt{\omega}$) the k_e and $\Delta i(E_s)_{r.m.s.}$ values can be calculated from equations (27) and (26) respectively.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

The $\Delta i \propto \sqrt{\omega}$ curves of best fit are shown in Figure 1.

Table 1 compares calculated and observed values of $\Delta i_{(E_p)_{r.m.s.}}$.

Fair agreement between theory and experiment is obtained up to ω_{\max} . Beyond this frequency, the electrochemical reaction lags more and more behind the alternating field changes and thus the theoretical treatment is no longer valid. A practically linear $\Delta i/\sqrt{\omega}$ relationship results for frequencies of up to 100 cycles. Similar results have been obtained previously by other investigators (Delahay 1952; Buchanan and Werner 1954).

The relative values of the equilibrium rate constants (k_e) for the reductions of Tl^+ , Cd^{++} , Pb^{++} , Sb^{+++} , Bi^{+++} ($10^{-3}N$ solutions in $0.5N$ HCl), and Fe^{+++} ($10^{-3}N$ solution in $0.1N$ ammonium oxalate) are shown in Table 2. It can be

TABLE 2
RELATIVE k_e VALUES OF CERTAIN IONIC REACTIONS OCCURRING AT THE DROPPING MERCURY
ELECTRODE CORRESPONDING TO THE RESPECTIVE HALF-STEP POTENTIALS
A.C. 15 mV r.m.s.; T , $20^\circ C$; cell impedance: 110 complex ohms

Supporting Electrolyte	Electrochemical Reaction	Ion Concn.	$\omega_{\max} \times 10^3$ (radn sec $^{-1}$)	$k_e \times 10^{-2}$ (cm sec $^{-1}$)
0.5N HCl	$Tl^+ + e \rightleftharpoons Tl$	$10^{-3}N$	3.14	9
0.1N Ammonium oxalate	$Fe^{+++} + e \rightleftharpoons Fe^{++}$	$10^{-3}N$	3.14	6.3
0.5N HCl	$Cd^{++} + 2e \rightleftharpoons Cd$	$10^{-3}N$	2.82	5.0
0.5N HCl	$Pb^{++} + 2e \rightleftharpoons Pb$	$10^{-3}N$	2.82	5.9
0.5N HCl	$Sb^{+++} + 3e \rightleftharpoons Sb$	$10^{-3}N$	1.88	4.8
0.5N HCl	$Bi^{+++} + 3e \rightleftharpoons Bi$	$10^{-3}N$	1.88	4.8

seen that the k_e values decrease progressively as the number of electrons involved in the reduction process increases. In other words, the electrochemical reaction becomes more irreversible with the increasing number of electrons transferred.

A notable feature of the experiments is the shifting of ω_{\max} towards lower frequencies with increasing impedance of the cell circuit (Kalyanasundaram 1951). The values of k_e reported in this paper refer to a cell impedance of 110 complex ohms.

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THE POLARIZATIONS OF LIQUIDS

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Summary

Equations suggested previously by Raman and Krishnan, Goss, Onsager, Böttcher, Frenkel, and Scholte are reviewed, and their applicabilities to observations by experiment are considered. Difficulties arise in estimating the dimensions of the cavity appropriate for a given molecule. It is shown that by taking this generally as ellipsoidal, with semi-axes a , b , and c , and computing the product abc from the molar volume at the melting point, a generalized Scholte equation gives satisfactory forecasts of the polarizations of liquids and vapours, and of the variations of the former with temperature and pressure, for a number of representative substances.

I. INTRODUCTION

The electronic or distortion polarizations (nP or $D P$) of liquids are in general slightly different from those of the corresponding vapours and often display a perceptible dependence upon temperature and pressure. The present paper is intended as a contribution to the problem of producing an equation by which these minor effects may be forecast and which will be useful in practice.

II. EXISTING THEORETICAL TREATMENTS

The first attempt to interpret the facts mentioned above was made by Raman and Krishnan (1928), who modified the Clausius-Mossotti relation towards greater applicability to non-polar liquids by introducing considerations of molecular anisotropy. They postulated that the internal field (polarizing the molecule) along any one of the principal directions, when the incident field E is in that direction, would be given by $E + k_1 P$ instead of $E + 4\pi p/3$, where k_1 are coefficients characteristic of the molecular form. If a , b , c are the semi-axes of the shape ellipsoid of the molecule,

$$k_1 = 2\pi abc \int_0^\infty \frac{ds}{(x^2 + s)\sqrt{(a^2 + s)(b^2 + s)(c^2 + s)}},$$

where x takes the values a , b , c respectively to give k_1 , k_2 , k_3 for the three principal directions. With this assumption, the Clausius-Mossotti relation becomes

$$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = P = \frac{4\pi N \alpha}{3} - \left(\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{N}{3} \sum \alpha_i s_i \right), \dots \dots \dots (1)$$

in which α_i are the principal polarizabilities and s_i are the factors $4\pi/3 - k_i$. Since, for positive values of s_i , α_i will be larger than for negative values, the second term (within parentheses) on the r.h.s. is always positive. Accordingly

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this treatment predicts that the polarization of a liquid should, in all cases, be smaller than that of the corresponding vapour, except when the molecule is spherical, when $P_{\text{liq.}} = P_{\text{vap.}}$. In fact, however, such a general relation does not hold good, and further the proposed effective field is questionable.

Goss (1935) showed that the differences forecast by the Raman-Krishnan theory alone would not explain those found by experiment, and introduced another term—called “false polarization”—into equation (1). Audsley and Goss (1941) expressed the relation as

$$P_{\text{vap.}} - P_{\text{liq.}} = \frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{N}{3} (\alpha_1 s_1 + \alpha_2 s_2 + \alpha_3 s_3) - Z \left(\frac{\varepsilon - 1}{\varepsilon + 2} \right)^4, \dots (2)$$

where the last term was said to arise from solvent effects, and could be deduced from the variation of the polarization of the substance with concentration in another solvent.

Kirkwood (1936) developed statistical formulae for dense non-polar gases, but an extension of his procedure to liquids would not be easy. Müller (1936) considered non-polar liquids, having restricted freedom of rotation of the molecules and a quasi-crystalline structure, but the effects of these conditions on the polarization cannot be evaluated directly without arbitrary postulates.

Onsager's (1936) theory for polar liquids is well known, but the argument involved therein would lead to the Clausius-Mossotti relation for non-polar liquids. Böttcher (1942), refining the treatment of Onsager, deduced the relation

$$\frac{(\varepsilon - 1)(2\varepsilon + 1)}{12\pi\varepsilon} = N \frac{d}{M} \frac{\alpha}{1 - [2\alpha(\varepsilon - 1)/a^3(2\varepsilon + 1)]},$$

for non-polar substances, where a is the radius of the cavity employed to calculate the cavity and reaction fields; he avoided Onsager's procedure of eliminating a . The above equation can be rewritten as

$$\frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{M}{d} = P = 4\pi N \alpha \frac{9\varepsilon}{(\varepsilon + 2)[2\varepsilon + 1 - (2\alpha/a^3)(\varepsilon - 1)]}, \dots (3)$$

He applied equation (3) to discuss the variation of the molar polarization of carbon disulphide (liquid) with pressure and pointed out that the value for the radius of the cavity, a , should be about equal to the radius of the molecule as calculated from the molar volume at absolute zero. However, it can readily be seen that this equation cannot satisfactorily explain the observed differences between the molar polarizations in the liquid and vapour states, unless α is taken as considerably different in the two cases. Böttcher suggested $a = 2.32 \text{ \AA}$ and $\alpha = 7.26 \times 10^{-24}$ for CS_2 in the liquid state, the latter being 16 per cent. less than the vapour value. If α is considered the same for vapours and liquids, the polarization in the liquid state calculated from (3) comes out considerably higher than the vapour value.

Frenkel (1946, p. 274) developed an equation for a non-polar liquid, taking into account the optical anisotropy of the molecule but not the anisotropy of

shape and the consequent anisotropy of the polarizing field. Neglecting saturation effects, that is, the terms involving E^2 , his equation (41) reduces to

$$\bar{p}_E = \frac{E}{3} \sum \frac{3\epsilon a^3 \alpha_1}{(2\epsilon + 1)a^3 - 2(\epsilon - 1)\alpha_1},$$

which with proper substitutions, can be written as

$$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = P = \frac{4\pi N}{3(\epsilon + 2)} \sum \frac{3\epsilon \alpha_1}{(2\epsilon + 1) - [2(\epsilon - 1)\alpha_1/a^3]}. \quad (4)$$

This equation also forecasts that the molar polarization in the liquid state will be higher than that in the vapour state, contrary to experimental facts, and is worse than equation (3) in this respect.

III. A RIGOROUS EQUATION FOR THE LIQUID STATE

Scholte (1949) developed a theory of the electric susceptibility of polar liquids, based upon the molecule as an ellipsoid, but with the simplification—on the lines of Böttcher's treatment of non-polar liquids—for the distortion polarization, that he neglected the anisotropy of polarizability as well as that of the field.

Anisotropy does play an important part in modifying pP , and in an equation for a non-polar liquid this cannot be neglected, though for a polar liquid, to disregard it may not have much influence on the calculation of μ , especially when ${}_0P$ is large. The considerations advanced by Scholte can lead to a rigorous equation for a non-polar liquid, but as far as the present authors are aware, no such equation has been expressed or discussed with reference to experimental data.

From Scholte, for an ellipsoidal cavity of semi-axes a, b, c situated in a medium of dielectric constant ϵ , the cavity field in any of the principal directions is given by

$$\frac{\epsilon}{\epsilon + (1 - \epsilon)A_1} E,$$

for an external field E in the concerned direction, where

$$A_1 = \frac{abc}{2} \int_0^\infty \frac{ds}{(s + x^2)\sqrt{[(s + a^2)(s + b^2)(s + c^2)]}},$$

x standing respectively for a, b, c . The reaction field of the ellipsoid is given by $f_1 m_1$, where m_1 is the moment induced in the particular direction and

$$f_1 = \frac{3A_1(1 - A_1)(\epsilon - 1)}{abc[\epsilon + (1 - \epsilon)A_1]}.$$

If the external field E is incident and making direction-cosines $\beta_1, \beta_2, \beta_3$ with the principal axes of the ellipsoid, the field in any of those directions is given by

$$E_1 = \frac{\epsilon}{\epsilon + (1 - \epsilon)A_1} \cdot E\beta_1 + f_1 m_1,$$

where $m_1 = \alpha_1 E_1$ (α_1 being the principal polarizabilities). Thus

$$E_1 = \frac{\varepsilon}{\varepsilon + (1 - \varepsilon)A_1} \cdot \frac{1}{1 - f_1\alpha_1} \cdot E\beta_1.$$

The induced moment in the direction of the incident field, per unit field, is given by

$$\frac{m}{E} = \sum \frac{\alpha_1 E_1 \beta_1}{E} = \sum \frac{\varepsilon}{\varepsilon + (1 - \varepsilon)A_1} \cdot \frac{\alpha_1}{1 - f_1\alpha_1} \cdot \beta_1^2,$$

Averaging for all orientations, neglecting orientational effects, and noting that

$$\overline{\beta_1^2} = \overline{\beta_2^2} = \overline{\beta_3^2} = \frac{1}{3},$$

and multiplying by n , the number of molecules per c.c., we get

$$\frac{n\bar{m}}{E} = \frac{\varepsilon - 1}{4\pi} = \frac{n}{3} \sum \frac{\varepsilon}{\varepsilon + (1 - \varepsilon)A_1} \cdot \frac{\alpha_1}{1 - f_1\alpha_1},$$

which can be modified as

$$\frac{\varepsilon - 1}{\varepsilon + 2} \frac{M}{d} = P = \frac{4\pi N}{3} \frac{\varepsilon}{\varepsilon + 2} \sum \frac{\alpha_1}{1 - f_1\alpha_1} \cdot \frac{1}{\varepsilon + (1 - \varepsilon)A_1}, \quad \dots (5)$$

where f_1 , it may be recalled, is

$$\frac{3A_1(1 - A_1)(\varepsilon - 1)}{abc[\varepsilon + (1 - \varepsilon)A_1]}.$$

That the above neglect of the orientational effects does not alter the distortion polarization can be seen from the general derivation of Debye's equation by van Vleck (1932, p. 32).

It is noteworthy that equation (5) for a non-polar liquid is the same as Frenkel's if

$$A_1 = A_2 = A_3 = \frac{1}{3}, \quad \text{and} \quad a = b = c,$$

and that Frenkel's equation is the same as Böttcher's if $\alpha_1 = \alpha_2 = \alpha_3$. The latter will reduce to the Clausius-Mossotti relation if $4\pi a^3/3 = 1/n_{c.c.}$

IV. DISCUSSION

(a) Application to the Polarization of Non-Polar Liquids

The value to be substituted for abc is still an open question. In the calculation of the structural factors A_1, A_2, A_3 relative values of a, b, c only are of consequence, and so the molecular dimensions can be used for that purpose. Further we require the absolute value of the product abc . Böttcher's conclusion that this product (in his case a^3) is of the order of that deduced from the molar volume at absolute zero is based on the application of his approximate relation to experimental data, and leads to very high values for the polarization in the liquid state, unless the polarizability is considered to be smaller than in the vapour state. So it is here suggested—though without theoretical justification—that $4\pi abcN/3$ may be set equal to the minimum volume in the liquid state,

namely the molar volume at the melting point. Thus, using $abc = 3M/4\pi Nd_{m.p.}$, where $d_{m.p.}$ is the density of a liquid at its melting point, experimental values of molar polarizations $(\epsilon - 1)M/(\epsilon + 2)d$ are, in Table 2, compared with the same calculated from equation (5), taking α as obtained from the vapour polarization. The values calculated—with the assumption that $a^3 = 3M/4\pi Nd_{m.p.}$ —from equations (4), (3), and (1) are also given. The polarizabilities α_1 , α_2 , α_3 are from Landolt and Börnstein's (1951) *Tabellen*, or from Audsley and Goss (1941), or from Le Fèvre and Le Fèvre (1954), but are proportionately changed to correspond to the mean α obtained from ${}_DP$ or ${}_EP$. The densities are taken from Timmermans (1950) and the $d_{m.p.}$'s in some cases secured by extrapolations.

TABLE 1
STRUCTURE FACTORS AND OTHER DATA FOR 12 COMPOUNDS

Compounds	A_1	A_2	A_3	P	$10^{24}a$	$10^{24}\alpha_1$	$10^{24}\alpha_2$	$10^{24}\alpha_3$	$d_{m.p.}$
Pentane ..	0.190	0.405	0.405	${}_DP$ 25.2*	10.00	12.40	8.80	8.80	0.7607
Hexane ..	0.170	0.415	0.415	„ 30.0†	11.91	14.85	10.44	10.44	0.7672
Heptane ..	0.150	0.425	0.425	„ 34.9†	13.86	17.52	12.03	12.03	0.7792
CCl_4 ..	1/3	1/3	1/3	„ 28.05‡	11.14	—	—	—	1.679
				${}_EP$ 25.82**	10.25	—	—	—	„
CS_2 ..	0.173	0.4135	0.4135	${}_DP$ 21.7‡	8.615	14.92	5.46	5.46	1.454
				${}_EP$ 20.03**	7.95	13.77	5.04	5.04	„
C_6H_6 ..	0.225	0.225	0.550	${}_DP$ 27.0¶	10.72	12.10	12.10	7.96	0.8924
				${}_EP$ 25.1**	9.96	11.24	11.24	7.40	„
cycloHexane	0.255	0.335	0.410	${}_DP$ 27.5¶	10.91	11.72	11.72	9.29	0.7906
$CHCl_3$..	0.460	0.270	0.270	„ 24.8§	9.845	7.99	10.77	10.77	1.643
				${}_EP$ 20.87**	8.285	6.73	9.06	9.06	„
CH_2Cl_2 ..	0.220	0.360	0.420	„ 15.97**	6.343	8.29	5.83	4.91	1.536
Acetone ..	0.235	0.315	0.450	„ 15.74**	6.25	7.01	6.99	4.75	0.9157
C_6H_5Cl ..	0.185	0.265	0.550	${}_DP$ 31.5	12.50	16.26	13.51	7.74	1.177
$C_6H_5NO_2$..	0.175	0.250	0.575	„ 37.2	14.77	20.30	15.14	8.86	1.217

* Kubo (1935).

† McAlpine and Smyth (1934).

‡ Le Fèvre and Rao (1954).

§ Ramaswamy (1936).

|| McAlpine and Smyth (1935).

¶ Le Fèvre and Rao (1955).

** See Table 4.

The structural factors A_1 originate from the approximate dimensions of the molecules given by Buckingham and Le Fèvre (1952), or Holland and Le Fèvre (1950), or Bhagavantam (1940, p. 75), being finally read from the graphs published by Osborn (1945). ${}_EP_{liq.}$ values in general are computed from the data in Landolt and Börnstein's *Tabellen* (5th Ed.). A_1 , α_1 , $d_{m.p.}$, etc. are listed in Table 1.

It can be seen from Table 2 that the polarizations calculated from equation (5) and the experimental ones are in quite good agreement except in the case of benzene. The temperature variations of the polarization—predicted and experimental—are of the same order, though not exactly equal.

(b) Application to the Variation of Polarization with Pressure

Equation (5) can also be applied to the variation of polarization with pressure. It is here used with Danforth's (1931) investigations on liquid CS_2 . In the elimination of abc , the density at the melting point, and the melting point itself, become different at different pressures. However, to carry the suggestion to its logical conclusion, melting points, and the approximate densities

TABLE 2
CALCULATIONS OF P BY VARIOUS EQUATIONS

	t (°C)	$\epsilon_{\text{liq.}}$	$d_{\text{liq.}}$	$P = \frac{\epsilon-1}{\epsilon+2} \frac{M}{d}$	P Calc. from (5)	P Calc. from (4)	P Calc. from (3)	P Calc. from (1)
Pentane* ..	30 -90	1.828 2.011	0.6163 0.7257	25.30 25.04	25.31 24.96	25.77 25.45	25.68 25.34	24.92 24.87
Hexane* ..	30 -90	1.875 2.044	0.6507 0.7533	29.88 29.51	29.97 29.55	30.63 30.26	30.51 30.12	29.59 29.53
Heptane* ..	30 -90	1.912 2.073	0.6755 0.7738	34.55 34.09	34.69 34.24	35.62 35.22	35.47 35.05	34.31 34.23
CCl_4^\dagger ..	0 70	2.2734 2.1478	1.6326 1.4963	28.06 28.44	28.19 28.47	28.19 28.47	28.19 28.47	28.05 28.05
$\text{C}_6\text{H}_6^\dagger$..	10 55	2.3024 2.2133	0.8895 0.8411	26.59 26.74	26.28 26.50	27.27 27.46	27.21 27.43	26.32 26.35
CS_2^\ddagger ..	20	2.6318	1.2632	21.23	21.07	25.01	22.6	20.35
cycloHexane ‡	20	2.022	0.7787	27.44	27.42	27.57	27.54	27.38

* Dornie and Smyth (1930).

† Le Fèvre (1938).

‡ Müller (1937).

at those temperatures for the various pressures are calculated. Melting points can be obtained approximately by the use of Clausius-Clapeyron equation

$$\frac{dp}{dT} = \frac{L}{T(v_2 - v_1)}$$

with $L=13.8$ cal, $T=-112^\circ\text{C}$ (Timmermans 1950), v_1 (solid) $=1/1.5539$, and v_2 (liquid) $=1/1.457$ (Landolt-Börnstein's (1923) *Tabellen*). The densities at these melting points and corresponding pressures are then obtained from the data of Bridgmann (1913). The calculated values of P are compared with the experimental ones in Table 3.

The calculated values for the lower pressures at 30°C are in discord with those from experiment. However, this reported variation of P_{CS_2} at lower pressures is not in agreement with the investigations of Chang (1935) and Kyropoulos (1926), and could not occur at the corresponding values of ϵ .

Böttcher's equation (3) also, with his suggested values $a=2.32 \text{ \AA}$ and $\alpha=7.26 \times 10^{-24}$, does not account for this anomalous variation. Except for this one discrepancy—in which the experimental values are doubtful—it can be seen from Table 3 that the present suggestion satisfactorily covers the variation of P with pressure, without recourse to the postulate that the polarizability changes with state.

TABLE 3
DEPENDENCE ON PRESSURE OF THE POLARIZATION OF CARBON DISULPHIDE

Temp. (°C)	Pressure (atm)	ϵ	d	$d_{m.p.}$	$P_{\text{expt.}}$	P Calc. from (5)
30	1	2.61	1.241	1.457	21.43	21.11
	500	2.74	1.291	—	21.65	—
	1000	2.82	1.332	1.504	21.59	20.85
	2000	2.94	1.394	1.523	21.45	20.70
	6000	3.23	1.550	1.596	20.94	20.35
	12000	3.52	1.689	1.689	20.58	20.13
Total change ..					0.85	0.98
75	1000	2.69	1.286	1.504	21.35	21.13
	2000	2.83	1.357	1.523	21.26	20.90
	6000	3.16	1.521	1.596	20.97	20.54
	12000	3.45	1.661	1.689	20.61	20.28
Total change ..					0.74	0.85

(c) Application to Electronic Polarization of Liquids

Equation (5) can be applied to refraction when ϵ is replaced by n_{∞}^2 , P by ${}_EP$, and α corresponds to the electronic polarizability of the liquid. Non-polar and polar dielectrics should be covered. However, it is thought advisable to derive ${}_EP_{\text{vap.}}$ from ${}_EP_{\text{liq.}}$ rather than the reverse, in view of the usefulness of such a computation in the evaluation of atomic polarizations. The latter are estimated in practice by subtracting from observed distortion polarizations ${}_DP$ the appropriate electronic polarizations ${}_EP$. Numerical illustrations have been given in this Journal by Le Fèvre and Rao (1954, 1955). Since ${}_DP$ is usually measured for the gaseous substance, the proper ${}_EP$ should be one also determined in this condition. Unfortunately, however, values of ${}_EP_{\text{gas}}$ are often lacking, and as an inexact substitute ${}_EP_{\text{liq.}}$ (i.e. R_{∞} —the extrapolated molecular refraction, cf. Le Fèvre 1953) is used perforce instead.

Equation (5), in conjunction with the fact that ${}_EP_{\text{vap.}}=4\pi N\alpha/3$ can be rearranged as (6):

$$\frac{{}_EP_{\text{vap.}}}{{}_EP_{\text{liq.}}} = \frac{n_{\infty}^2 + 2}{n_{\infty}^2} \left[\alpha / \Sigma \frac{\alpha_1}{(1 - f_1 \alpha_1)(n_{\infty}^2 + (1 - n_{\infty}^2)A_1)} \right]. \quad \dots \quad (6)$$

Strictly, of course, the α_1 's should be drawn from data referring to gases, but when they are unknown the approximation of using polarizabilities secured in the liquid state may be safely adopted (since the r.h.s. of (6) is a ratio of the order of unity). Accordingly the ϵP 's and α_1 's in Table 1 are those for the liquid state. Values of ϵP_{vap} , calculated via (6), with the aid of necessary constants

TABLE 4
CALCULATION OF ϵP BY EQUATION (6)

Compounds	t (°C)	n_{∞}^2 Liquid	d_4^t	$\epsilon P_{\text{liq.}}^\dagger$	ϵP_{gas} Calc. from (6)	ϵP_{gas} Observed
CS ₂	15.7	2.505	1.2700	20.02	20.73	20.40
CCl ₄	20	2.092	1.5912	25.82	25.64	25.83
C ₆ H ₆	20	2.181	0.8791	25.10	25.75	26.2†
CHCl ₃	15	2.065	1.4985	20.87	20.86	21.05
CH ₂ Cl ₂	20	1.995*	1.3247	15.97	15.97	16.04
Acetone	19.4	1.819	0.7912	15.74	15.70	16.04

* Vogel (1948).

† $\epsilon P_{\text{liq.}} = M(n_{\infty}^2 - 1)/(n_{\infty}^2 + 2)d$.

‡ McAlpine and Smyth (1933).

from Table 1, are compared, in Table 4, with the ϵP 's by experiment. (The last-named are in general based on observations listed in Landolt-Börnstein's *Tabellen* (5th Ed.)); the n_{∞}^2 values are also from the same source.

TABLE 5
 μ -VALUES FOR THREE COMPOUNDS

Compounds	T (°K)	ϵ	d	$\mu_{\text{calc.}}$ from (7)	μ (Scholte)	$\mu_{\text{vap.}}$ (Expt.)
CHCl ₃ *	293	4.813	1.489	0.99	1.08	1.02
C ₆ H ₅ Cl*	302.2	5.475	1.096	1.67	1.63	1.71
C ₆ H ₅ NO ₂ †	298	34.89	1.199	4.93	5.04	4.2

* Values as used by Scholte (1949).

† From Le Fèvre (1938).

(i) *Application to Polar Liquids*.—When the present suggestions are incorporated, Scholte's (1949) equation for polar liquids becomes

$$\frac{\epsilon - 1}{4\pi} \cdot \frac{M}{d} = \frac{N}{3} \left[\sum \frac{\epsilon}{1 + (1 - \epsilon)A_1} \cdot \frac{\alpha_1}{1 - f_1\alpha_1} \right] + \frac{N\mu^2}{3kT} \cdot \frac{\epsilon}{\epsilon + (1 - \epsilon)A_1} \cdot \frac{1}{(1 - f_1\alpha_1)^2}, \quad \dots \dots \dots (7)$$

where α_1 and A_1 are the polarizability and structural factor respectively in the direction of the permanent moment μ , and f_1 is as defined under equation (5).

Scholte suggested obtaining the product abc (considered as a^3) by applying Böttcher's equation (3) to the variation of refraction with temperature. When the present proposal for abc is adopted in conjunction with equation (7), μ for three compounds emerges as shown in Table 5. Thus this procedure seems to give slightly better values than does that of Scholte.

V. GENERAL CONCLUSION

The use of the molar volume at the melting point for the elimination of abc , while having no special theoretical significance, seems appropriate for a number of compounds. This fixed value of abc is capable of accounting for the change of polarization with temperature in a small range when the variation of ϵ is also small; when larger alterations of ϵ are produced by the use of high pressures, it is found necessary to conclude that abc is decreasing. Further, the dipole moments of liquids having low dielectric constants can be predicted accurately, whereas for nitrobenzene (with $\epsilon=35$), $\mu_{\text{calc.}}$ is far from the correct value. It can be seen that, were a smaller value of abc taken for nitrobenzene, much better agreement would be obtained. These general tendencies suggest that the theory for liquids needs a further refinement to include some sort of molecular interaction depending upon ϵ .

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INTENSITY DISTRIBUTION IN LONG-SPACING X-RAY PATTERNS OF A SERIES OF EVEN LONG-CHAIN *n*-ALCOHOLS AND *n*-ACIDS

By J. FRIDRICHSONS*

[Manuscript received January 18, 1955]

Summary

Characteristic intensity variations in long-spacing patterns of even alcohols and acids with chain lengths of 20 to 28 are described. The variations are related to the carbon number of the chain and could therefore be used for rapid identification of these long-chain compounds.

I. INTRODUCTION

Since Müller's classical investigations on the long-spacing X-ray patterns (00 ℓ reflections) of long-chain compounds and the establishment of the linear relationship of the long-spacing value and carbon number in each homologous series, extensive use has been made of these spacings in the study of such compounds. Mainly by the work of Piper, Francis, Malkin, and co-workers, the determination of the long-spacing values has been developed to a sensitive method for identification of various long-chain compounds.

The early patterns of *n*-alcohols and acids revealed also an alternation in the intensity of odd and even orders of the long-spacing reflections (the odd terms being the stronger) which Shearer (1925) explained by assuming constant scattering power along the chain, with a decrease at one end (H) and an increase at the other (OH or COOH groups). However, patterns obtained later, extending to higher numbers of orders, showed the Shearer intensity rule to hold only for lower orders, as in the higher orders the even terms became stronger (Piper, Chibnall, and Williams 1934). This would indicate that in calculating the intensities of the 00 ℓ reflections the chain carbons had to be regarded as individual scattering centres.

In carrying out routine identification and purity tests for a series of even normal alcohols and acids by means of their long-spacing values, diffraction patterns with long-spacing reflections extending to very high orders ($\ell=20$ to 30) were obtained showing clearly certain characteristic intensity variations in the sequence of reflection orders that could be related with the number of carbon atoms in the chain. Although these variations certainly must have been observed before, it was considered worthwhile to describe them here, in view of their possible use for identification purposes.

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II. EXPERIMENTAL

The compounds investigated were even *n*-alcohols and their derived acids isolated from wool-wax (Murray and Schoenfeld 1955), and ranging in carbon number from $N=20$ to $N=28$ (denoted further on as C_{20} , C_{22} , C_{24} , C_{26} , and C_{28}).

The X-ray diffraction patterns were obtained in the usual way by pressing the sample material (in the form of crystalline flakes) on plane glass strips to orientate the basal (001)-planes of the crystals. A flat-film camera with a

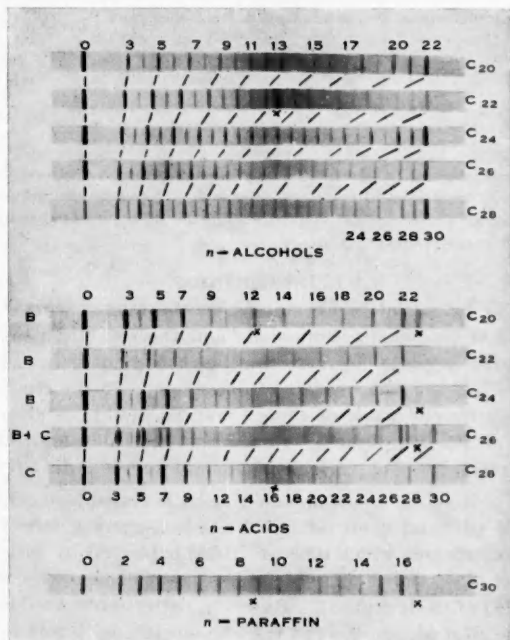


Fig. 1.—Diffraction patterns of alcohols and acids.

film-specimen distance of 80 mm and oscillation range of 15° was used first, for measuring the long-spacing values, and later on a 14.3 cm diameter powder camera, to record the long-spacing orders up to $\theta=25^\circ$. With Ni-filtered Cu-radiation (40 kV, 15 mA) and a slit collimator of 3 by 0.2 mm the average exposure times were 2–6 hr, depending on the size and composition of the specimen.

III. RESULTS

Measurement of the long-spacing values showed that all the five alcohols were in the *B*-form (Francis, Collins, and Piper 1937) and with a high degree of purity (no traces of other long-spacing reflections, spacing values on straight line). As to the acids, C_{20} and C_{24} were in the *B*-form (loc. cit; see also Francis

and Piper 1939), C_{28} in *C*-form (with faint traces of first *B*-spacing orders), C_{22} in *B*-form (with few orders of *C*-spacing), and C_{26} a mixture of both *B*- and *C*-forms.

As can be seen from Figure 1, which is a reproduction of the actual patterns obtained in the powder camera, there is a pronounced difference in the intensity distribution of the long-spacing orders in the alcohol and acid patterns. (In all patterns the first two orders of the sequences are cut off by the beam-stop. A few short-spacing reflections appearing in some patterns can be easily distinguished by their different form in the original films and are marked with crosses in Fig. 1. For comparison, the characteristic pattern of a *n*-paraffin, that of triacontane (C_{30}), is also shown in Fig. 1).

In the alcohol patterns the Shearer intensity variations are apparent up to a rather high term order, the odd and even orders becoming gradually equal in intensity in the region around $\theta=15^\circ$, and then the even orders begin to increase in intensity more rapidly. In the acid patterns there is a rapid decrease and subsequent increase of even term intensities, the minimum occurring at a rather low diffraction angle, and the odd order intensity also decreasing more rapidly

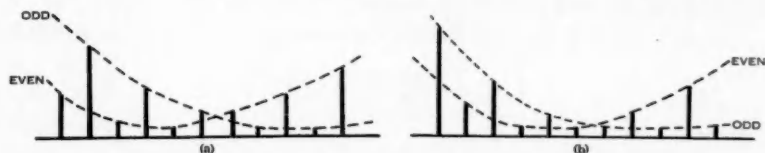


Fig. 2.—Schematic representation of odd-even term intensity changeover in acid patterns.

than in the alcohol patterns. A pair of adjacent odd and even terms with approximately equal intensities can be easily recognized, flanked on both sides either by two weaker or two stronger terms (as represented schematically in Fig. 2 (a) and (b)). In the acids C_{20} and C_{24} the changeover is distinctly of the type (a) of Figure 2, the term numbers of the pair being 9-10 and 11-12 respectively. In C_{28} too, although it is in the *C*-form, the changeover is of the same type and occurs at the term pair 13-14. In C_{22} the terms 10 and 11 are the weakest, so that here the changeover is of the type (b) of Figure 2. In C_{26} unfortunately term 11 of form *C* overlaps with term 12 of form *B*, but orders 12 and 13 of form *C* are the weakest.

IV. DISCUSSION

It appears therefore, that, at least for chain lengths between 20 and 28 carbon atoms, in the even acids of forms *B* and *C* the numbers of the term pair at which the even and odd order intensities change over, can be expressed in terms of the carbon number N as

$$l = \frac{1}{2}(N-2) \text{ and } l = \frac{1}{2}N.$$

Another characteristic peculiarity of both the alcohol and acid patterns is the abrupt decrease of intensity after the order $N+2$. It has been known (Pollard, Chibnall, and Piper 1933) that pure long-chain compounds give very

strong reflections in the order N and $N+2$, but as can be seen from Figure 1, there is also in this region a marked difference between the alcohol and acid patterns.

In the acid patterns, the odd terms practically disappear after the change-over, so that only the even terms are visible, the orders N and $N+2$ being the most intense, with a relatively weak order $N+1$ between them. In the alcohol patterns on the other hand, as already mentioned, the change of intensities is more gradual, so that all terms appear, the odd ones becoming weaker only at diffraction angles over 15° . The orders N and $N+1$ are approximately equal and $N+2$ exceptionally strong. After the order $N+2$ a number of relatively weak terms appear in the acid patterns up to the limiting oscillation angle, whereas in the alcohol patterns no higher term than $N+2$ is visible.

A similar abrupt decrease in intensity is apparent also in the paraffin pattern of Figure 1. Here the last strong term is $\frac{1}{2}(N+2)$, due to the fact that the c -axis spacing contains only one molecular length.

Some preliminary approximate calculations were carried out to relate the observed intensity variations with the chain structure of the molecule and its orientation in the unit cell of the crystal.

The intensities of the long-spacing reflections are given by the expression

$$I_{00l} = k \frac{1 + \cos^2 2\theta}{\sin 2\theta} \cdot F_{00l}^2,$$

where

$$F_{00l} = \sum f_n \cdot \cos 2\pi l z_n / c$$

is the structure amplitude of the molecule for the reflection $00l$ (f_n —atomic scattering factor of the n th atom, z_n —the z -coordinate of the n th atom in the unit cell of axial length c , with the origin at a centre of symmetry). The F -values for the $00l$ reflections were calculated for a number of trial models of the alcohol and acid chains (for $N=20$) with different orientations in the unit cell, to find the configuration which gave the best agreement between the calculated and observed intensity values.

Assuming as a first approximation a plane zigzag chain with a mean carbon-carbon distance of 1.54 \AA and a tetrahedral angle between them, the structure amplitudes F_{00l} will depend on the angle of tilt of the chain relative to the (001) -plane, the z -coordinates of the first carbon atom and the oxygen atoms, and finally, also on the angle of twist of the chain plane, defined by the angle between the chain plane and the plane containing the chain axis and the normal to the basal plane (001) . The angle of tilt can be determined directly from the increment of long-spacing values for adjacent members in the homologous series, given by the linear graph of spacing-values *versus* carbon number. For the B -form acids and alcohols this increment, d , is 2.33 and 2.09 \AA (from present data and Francis, Collins, and Piper's (*loc. cit.*) values), which, with a distance of 2.52 \AA between alternate carbon atoms in the chain would give tilt angles of 67.6 and 56° respectively. The approximate configuration of the molecule then follows from the average values given in the literature for the bond lengths

and angles in the end-carboxyl or end-hydroxyl group and in the case of the acids the position of the chain is to some extent fixed by the fact that two molecules are linked across a centre of symmetry by hydrogen bonds $-O-H-O=$. For a definite trial model the z -coordinates of all atoms then depend on the angle of twist of the molecular plane. The finally used values of bond lengths and angles are given in Figure 3, which shows the postulated configuration of the chains for twist angle 0° .

Structure amplitudes F were calculated for twist angles $0, 60, 90, 120$, and 180° (omitting the bonding hydrogen and end hydrogen, and regarding the CH_2 groups as single scattering centres).

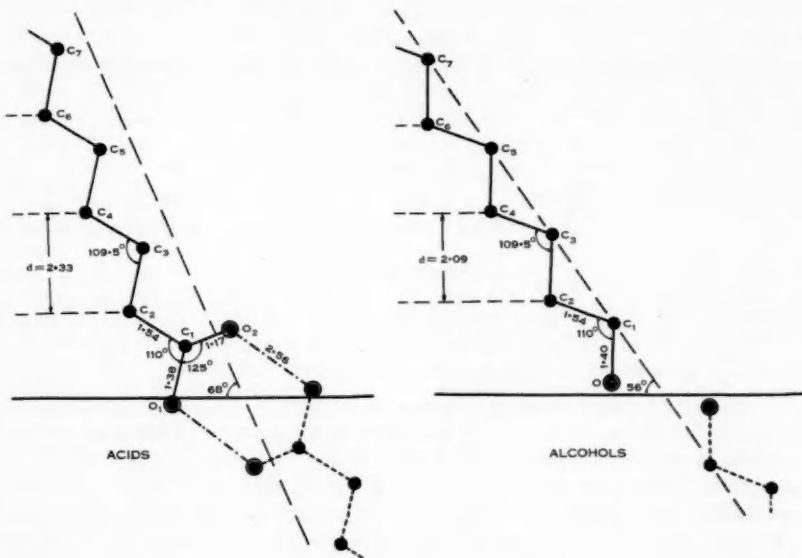


Fig. 3.—Alcohol and acid chain models.

A quantitative agreement is hardly to be expected for these preliminary calculations. Firstly, the assumption of a straight chain with tetrahedral angles and C—C distances of 1.54 \AA cannot be warranted without a complete single-crystal analysis. Vand, Morley, and Lomer (1951) have found that in lauric acid ($N=12$) the chain is slightly bent, indicating departures from the tetrahedral angles and normal C—C distances, and such a bend might be expected to occur even more in the longer chain compounds. Detailed analyses of other long-chain compounds (e.g. dicarboxylic acids, Morrison and Robertson 1949, pp. 980, 987, 999) have also shown that the bond lengths and angles vary considerably along the chain. Such variations would cause a deviation of d from the straight-chain constant value (Fig. 3) used here for the calculation of structure amplitudes F .

Secondly, the approximation in regarding the CH_2 groups as single scattering centres can also introduce appreciable errors in the calculated F -values in the case of a tilted and twisted chain, in view of the high percentage of hydrogen.

The experimental intensities too can be regarded only as approximately comparable with the calculated intensities, because they have been estimated only visually and no account has been taken of the shape of the specimen and absorption errors.

Nevertheless, for twist angles of 60° , the qualitative agreement in the general trend of calculated intensity variations with the peculiarities in the patterns is quite satisfactory, as can be seen from Table 1, which shows the values for acid C_{20} .

TABLE 1
CALCULATED AND OBSERVED RELATIVE INTENSITIES OF 00 l REFLECTIONS FOR n -ACID C_{20} (TWIST ANGLE 60°)

Order	$I_{\text{calc.}}$	$I_{\text{obs.}}$	Order	$I_{\text{calc.}}$	$I_{\text{obs.}}$	Order	$I_{\text{calc.}}$	$I_{\text{obs.}}$
3	280	300	11	1	3	19	2	0
4	27	20	12	13	15	20	45	50
5	105	150	13	0	0	21	7	4
6	3	2	14	14	15	22	50	60
7	30	50	15	0	0	23	8	?
8	1	2	16	12	13	24	10	3
9	8	15	17	0	0	25	8	0
10	7	10	18	10	15			

The very strong intensity of order $N+2$ in the alcohol patterns can be explained by the contributions of the identical CH_2 groups (spacing d), which are almost exactly in phase for $l=N+2$. In the acids the spacing d results in maximum cooperation for $l=N$ and $l=N+2$, so that both those reflections are strong. The steeper decrease of intensities at lower diffraction angles and the appearance of a well-defined pair of adjacent terms with nearly equal intensities in the acid patterns are caused by the contribution of the second oxygen.

V. CONCLUSION

As already mentioned the observed characteristic intensity variations suggest their possible use for rapid preliminary identification of normal long-chain compounds without precision measurements of the spacing values, at any rate in the range of carbon chain lengths examined, provided the materials are in sufficiently pure form to give long-spacing patterns with a large number of orders. (A large number of orders is essential also in any pattern intended for precision measurement of spacing values.) The diffraction pattern can be obtained very easily in any powder camera having an oscillation movement of approx. 25° (for Cu-radiation). If the sample is in well-developed flakes, gently pressed specimens will usually give only the long-spacing patterns, from which at a glance it can be decided whether the material is an acid, alcohol, or paraffin.

Next, the number of carbons in the chain can be determined simply by counting the order of the last strong reflection (order $N+2$) and in the case of acid patterns also from the order number of the adjacent pair of even and odd terms at which the intensity changeover occurs (terms $\frac{1}{2}(N-2)$ and $\frac{1}{2}N$). (The number of first few orders cut off by the beam-stop can be easily deduced from the trace of the direct beam on the film.)

As only even-numbered members of the series were available it would be of interest to verify whether the same or similar intensity variations are present in long-spacing patterns of odd n -compounds and compounds with shorter and longer chain lengths. For shorter chain lengths it can be expected that the relationships will be different, and indeed the single-crystal structure analysis of form C of lauric acid (Vand, Morley, and Lomer 1951) and the long-spacing pattern of stearic acid (Velick 1944) show that the changeover pair for the former (C_{12}) is 6 and 7 and for the latter (C_{18}) 9 and 10, or $\frac{1}{2}N$ and $\frac{1}{2}(N+2)$ respectively. In both these acids, too, the last two strong terms are still the terms N and $N+2$.

VI. ACKNOWLEDGMENTS

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AN INFRA-RED SPECTROSCOPIC STUDY OF NAPHTHALENE SUBSTITUTION

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Summary

Infra-red spectroscopic data on a number of mono- and disubstituted naphthalene derivatives have been obtained in the range 670–900 cm^{-1} , in order to test the validity of the substitution rules based upon the hydrogen bending vibrations in this region and the number of adjacent hydrogen atoms in the molecules.

It was found that the rules based on benzene substitution are generally valid for groups of two, three, or four hydrogen atoms in the naphthalene nucleus, although substituents which interact with the ring tend to widen the limits within which a band may be expected to fall. In the case of a single hydrogen atom the relevant bands are often weaker and their position variable.

I. INTRODUCTION

The characterization of substituted benzenes by means of the strong absorption bands in the infra-red spectra of these compounds between 670 and 900 cm^{-1} is well known and has been adequately discussed (Barnes *et al.* 1944; Whiffen and Thompson 1945; Whiffen, Torkington, and Thompson 1945; Richards and Thompson 1948; Colthup 1950; and Bellamy 1954).

The bands arise from the out-of-plane bending vibrations of the hydrogen atoms attached to the nucleus and rules have been formulated which relate the number of adjacent hydrogen atoms with the position of corresponding absorption peaks. These rules have been summarized by Colthup (1950) as follows:

5 adjacent H atoms (e.g. monosubstituted):	700 and 740 cm^{-1}
4 adjacent H atoms (e.g. <i>ortho</i> -disubstituted):	750 cm^{-1}
3 adjacent H atoms (e.g. <i>meta</i> -di-, or <i>vic.</i> -trisubstituted):	780 cm^{-1}
2 adjacent H atoms (e.g. <i>para</i> -di-, or <i>as</i> -trisubstituted):	820 cm^{-1}
1 single H atom (e.g. <i>meta</i> -di-, or <i>s</i> -trisubstituted):	860 cm^{-1}

Where a combination of two possibilities occurs in the one compound as in *meta*-disubstitution, for example, one finds that both bands occur, each being independent of the other. It would appear therefore, that the position of substituents could be unequivocally determined without difficulty, and while this is often the case, nevertheless difficulties are sometimes encountered when dealing with substituents which interact with the ring as these cause shifting of the bands (Randle and Whiffen 1952; Bellamy 1954).

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It is known that the out-of-plane bending vibrations of the hydrogen atoms attached to other aromatic nuclei also give rise to bands in this region but fewer studies have been made of the application of similar rules to such systems. Such studies have been mainly confined to hydrocarbons (Orr and Thompson 1950; Thompson *et al.* 1950; Cannon and Sutherland 1951; Broomfield 1952; Kamada 1952) and little attention has been paid to the effect of non-hydrocarbon substituents. Further studies are highly desirable as the information obtained will indicate the degree of reliance which may be placed on any attempted characterization of substituted polynuclear systems.

In the present paper, therefore, data are presented on a number of mono- and disubstituted naphthalene derivatives and these data are examined for correlations which would allow the position of the substituents to be inferred.

II. EXPERIMENTAL

The compounds studied were laboratory samples, the majority of which were prepared in connection with other work and were kindly presented to the authors. The samples were examined when solid, as paraffin oil pastes, at two thicknesses where necessary in order to bring out details of the spectra. In the case of liquid samples, capillary films were found satisfactory. The spectra were obtained between 670 and 900 cm^{-1} with a Perkin-Elmer Model 12-C infra-red spectrometer using a sodium chloride prism and 13-cycle amplifier. Calibration was effected in the usual manner using the data of Oetjen, Kao, and Randall (1942) for the absorption bands of ammonia and carbon dioxide. The intensities were estimated by comparison with the background produced by a single sodium chloride plate.

III. DISCUSSION

The spectra are presented in the form of line graphs in Figures 1 to 4. Included in the graphs are the wave numbers of the bands which have been assigned to the out-of-plane bending vibrations. In analysing the spectra the assumption made by previous authors has been used; namely, that the system will behave to a first approximation as if it were two benzene rings, both *ortho*-disubstituted. A correlation chart is included (Fig. 5) which shows the position normally to be expected for the bands of each arrangement of substituents. Where only a few compounds were available, the range has been extended somewhat. Dotted lines indicate less reliable correlations.

(a) Monosubstituted Derivatives

In the case of monosubstituted naphthyl derivatives (Fig. 1) only two arrangements are possible. The α -derivatives have groups of four and three adjacent hydrogen atoms while the β -derivatives have groups of four and two adjacent atoms and a single hydrogen. In the α -alkylnaphthalenes reported by Broomfield (1952) the band corresponding to four hydrogens occurs in the range 775–780 cm^{-1} . Data on α -methyl- to α -*n*-pentylnaphthalene were available in the set of A.P.I. spectrograms. In this region, however, the cell thickness used resulted in complete absorption so that this band was not measured separately from the nearby band at 790 cm^{-1} , except in the case of α -methyl-naphthalene (No. 762) where these were recorded at 777 and 795 cm^{-1} . With

substituents other than alkyl, however, the values drop slightly to the region around $760\text{--}770\text{ cm}^{-1}$ so that the range $760\text{--}780\text{ cm}^{-1}$ encompasses all the samples measured. The three adjacent hydrogen atoms in the same ring as the substituent give rise to a strong band normally close to 790 cm^{-1} . Change of state appears to have little effect but unsaturated groups cause the band to shift to about 800 cm^{-1} . As expected no strong bands common to all compounds are found between the limits studied other than these two.

The β -naphthalenes similarly exhibit a strong band due to the four hydrogen atoms but the frequencies in this case are somewhat lower, lying generally in the range $740\text{--}750\text{ cm}^{-1}$. In one case, β -iodonaphthalene, the band is at 735 cm^{-1} and in a few others nearly to 760 cm^{-1} . It may be significant that both β -CN

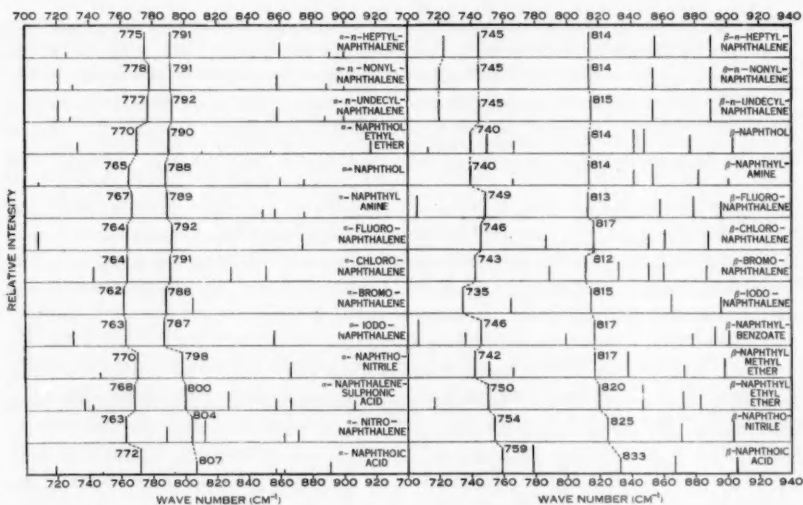


Fig. 1.—The infra-red absorption bands of monosubstituted naphthalene compounds in the range $700\text{--}900\text{ cm}^{-1}$. The values for the alkynaphthalenes are taken from Broomfield (1952).

and β -COOH have values towards the top of the range. That the α - and β -substituents affect the opposite ring differently is well known from other work (Bryson 1951), and indicates that a treatment of the system as two separate benzene rings may have limitations.

The two adjacent hydrogen atoms give rise to a strong band between 810 and 835 cm^{-1} but again β -CN and β -COOH give the higher values within this range. By analogy with benzene compounds, β -naphthalene derivatives should also exhibit a band between 850 and 880 cm^{-1} due to the single hydrogen atom. There is, in fact, a series of bands of medium intensity between 850 and 875 cm^{-1} but a second series occurs in the range $875\text{--}905\text{ cm}^{-1}$ and although these are also of medium intensity, in some cases they are stronger than the lower frequency bands.

(b) *Disubstituted Derivatives*

Disubstitution of the naphthalene nucleus gives rise to 10 arrangements, four of which are mononuclear substituted (1,2, 1,3, 1,4, and 2,3) while six are binuclear substituted (1,5, 1,6, 1,7, 1,8, 2,6, and 2,7). It is convenient to discuss the mononuclear substituted group first (Fig. 2).

Only four 1,4-disubstituted compounds were available and in these a strong band was found between 755 and 765 cm^{-1} , clearly due to the unsubstituted ring. A second band occurred in the interval between 820 and 830 cm^{-1} due to the hydrogen atoms in the 2,3-positions.

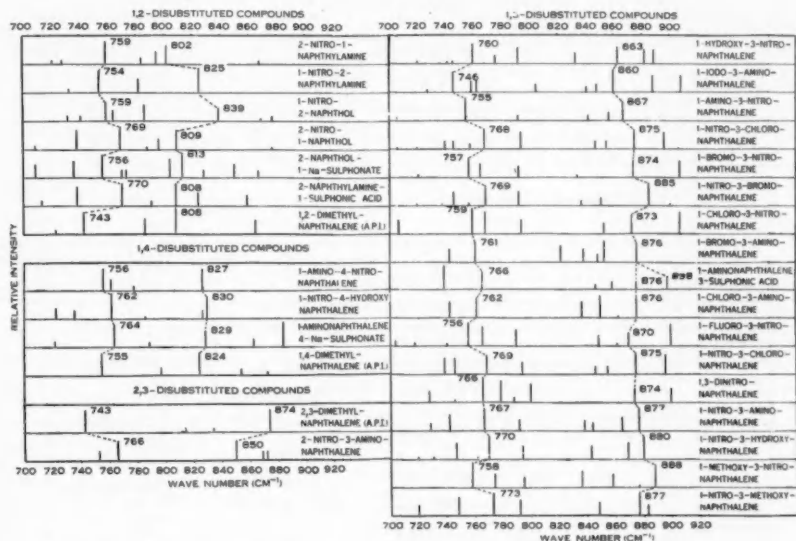


Fig. 2.—The infra-red absorption bands of 1,2-, 1,3-, 1,4-, and 2,3-disubstituted naphthalene compounds in the range 700-900 cm^{-1} .

Altogether 17 of the 1,3-compounds were available which allowed a better estimate of the influence of two substituents to be made. The lower frequency band is strong and falls in the range 745-775 cm^{-1} as expected. Within this range the 3-nitro-compounds lie towards the bottom of the range. The single hydrogen atom produces a band between 860 and 890 cm^{-1} . Only one compound seems doubtful, namely, 1-amino-3-sulphonic acid and in this case, although bands do fall in the range indicated, there are other bands nearby (at 739 and 898 cm^{-1}) which could be due to the hydrogen atoms. Furthermore the presence of a nitro group in either the 1- or 3-position apparently gives rise to a band characteristic of this group near 790 cm^{-1} .

The 1,2-disubstituted arrangement gave bands at 740-770 cm^{-1} and 800-840 cm^{-1} . These latter bands due to the two adjacent hydrogen atoms

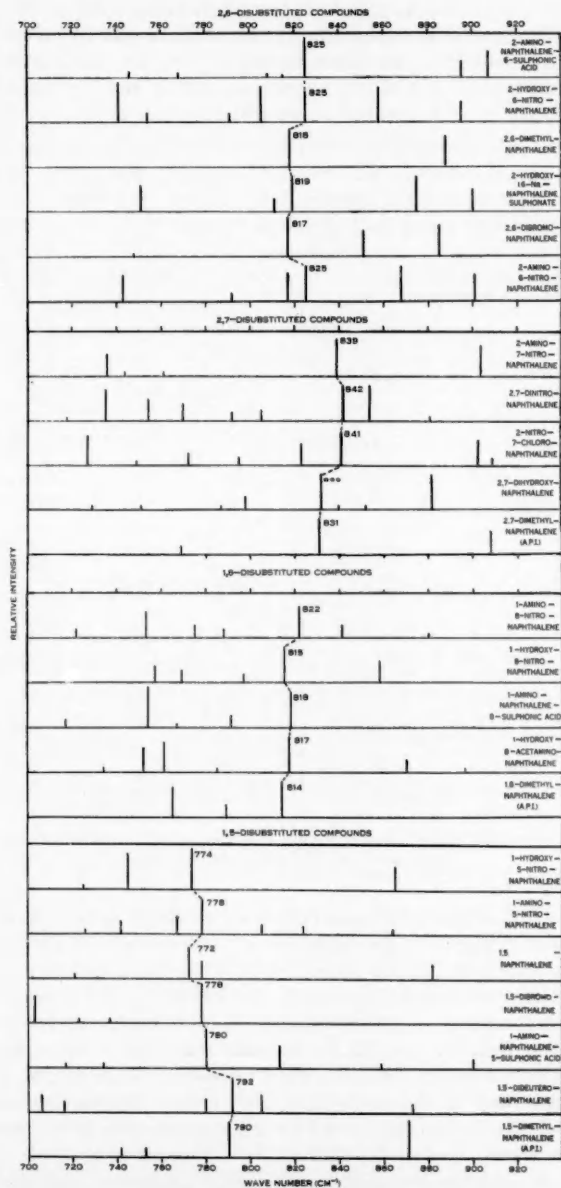


Fig. 3.—The infra-red absorption bands of 2,6-, 2,7-, 1,8-, and 1,5-disubstituted naphthalene compounds in the range 700–900 cm⁻¹.

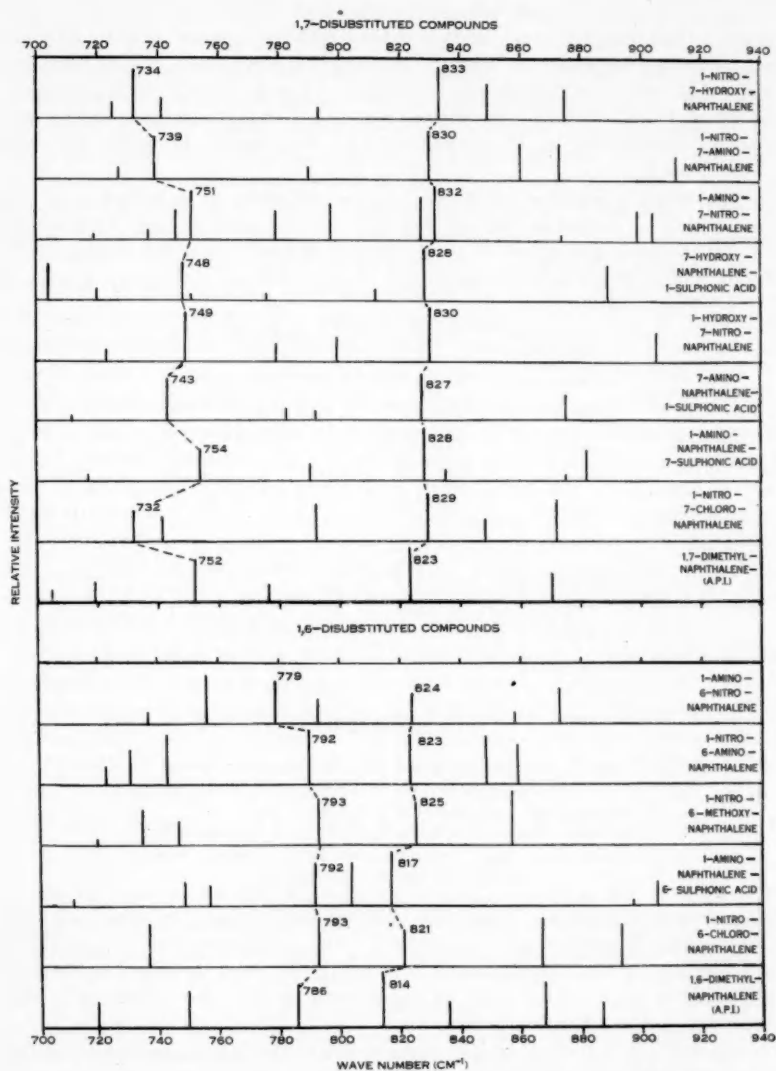


Fig. 4.—The infra-red absorption bands of 1,6- and 1,7-disubstituted naphthalene compounds in the range 700–900 cm⁻¹.

occurred in all but one compound between 800 and 830 cm^{-1} , the only exception being 1-nitro-2-naphthol at 839 cm^{-1} . This high value does not appear to be related to the intramolecular hydrogen bonding which occurs in this compound since 2-nitro-1-naphthol is normal (809 cm^{-1}). Only two 2,3-disubstituted compounds were available (ranges 740–770 cm^{-1} and 850–875 cm^{-1}), but these conformed to expectation. It will be observed that of the mononuclear disubstituted compounds it is impractical to distinguish between 1,3- and 2,3-compounds.

The seven 1,5-disubstituted compounds exhibited, as expected, only one band, which lay between 770 and 795 cm^{-1} . The values 792 cm^{-1} (didentero) and 790 cm^{-1} (dimethyl) are in good agreement with values for benzene compounds having three adjacent hydrogen atoms and are apparently typical of

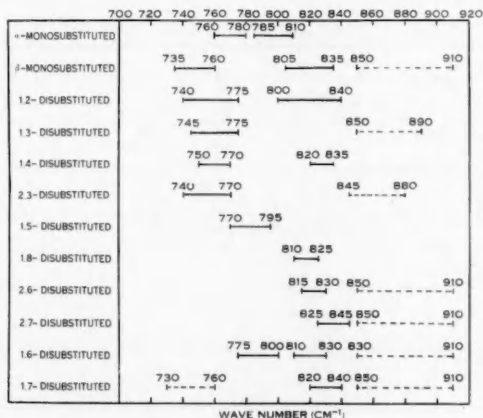


Fig. 5.—Correlation chart showing the regions of absorption of the hydrogen bending vibrations of the mono- and disubstituted naphthalene derivatives.

In cases where only a few compounds were available the ranges have been extended somewhat. Dotted lines indicate less reliable correlations.

those cases in which little interaction with the ring occurs. In other cases the values appear to drop about 10–15 cm^{-1} . The 1,8-compounds are related to the 1,5-group in that both possess two groups of three adjacent hydrogens. Once again a single strong band is found but this time the values are higher in the range 810–825 cm^{-1} .

The 2,6- and 2,7-arrangements are also related in that each has two groups of two adjacent hydrogen atoms and two single hydrogen atoms. In both types the lower frequency band is strong and sharp, occurring in the range 815–825 cm^{-1} for the six 2,6-compounds examined and in the range 830 to 845 cm^{-1} for the five 2,7-compounds. The single hydrogen atom gives a band of variable intensity (generally medium) and these are found in the rather wide range 850–910 cm^{-1} .

The band in the 2,6-disubstituted compounds is particularly difficult to correctly assign as frequently more than one band occurs within the possible range.

The 1,6- and 1,7-compounds should produce three bands, due to a single hydrogen, a group of two and a group of three. The lower frequency bands of the 1,6-compounds are fairly readily distinguished lying in the range $775\text{--}795\text{ cm}^{-1}$ for the three and $810\text{--}825\text{ cm}^{-1}$ for the two hydrogen atoms. Again the higher frequency band due to the single hydrogen is most uncertain and in the case of 1-amino-6-sulphonic acid is either the medium band at 905 cm^{-1} or is entirely absent. The 1,7-compounds appear to be anomalous. They all possess a strong band apparently due to two hydrogen atoms in the range $820\text{--}835\text{ cm}^{-1}$. The low frequency band due to three atoms adjacent seems to be abnormally displaced to lower frequencies and its intensity is much less than normally expected. The single hydrogen atom gives rise to a band of medium intensity only, the position of which is variable as in the case of other arrangements similarly possessing a lone hydrogen.

The general conclusion to be reached is that the correlation rules developed for benzenoid compounds may be usefully applied to naphthalene compounds for the purpose of indicating the arrangement of substituents. Exceptions, however, occur and the possible ranges in which bands are to be found overlap to some extent. Thus, in practice, it will probably be found that the method operates to reduce the number of possible configurations to two or three rather than specifically indicating one arrangement. When making such an analysis bands due to two, three, or four adjacent hydrogen atoms should be sought since the band due to a single hydrogen atom is rather unreliable.

Because of interaction in the solid, small differences in wavelength due to the nature of the substituent are difficult to detect. A study of such effects would be best accomplished in solution but this raises a real difficulty with polar compounds for which a suitable solvent must be found. That such shifts may be detected can be seen from the data of Ferguson and Werner (1954) on the α - and β -monohalogenonaphthalenes where the increased size of the halogen affects the vibration of the hydrogen atoms even in the other ring.

IV. ACKNOWLEDGMENTS

The authors would like to express their appreciation to Mr. A. Bryson for making available a large number of disubstituted compounds. Professor D. P. Craig also kindly provided some of the samples examined.

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THE INFRA-RED SPECTRA OF THE BORATE ESTERS

By R. L. WERNER* and K. G. O'BRIEN†

[Manuscript received March 24, 1955]

Summary

The infra-red spectra of a series of alkyl and aryl esters of boric acid have been obtained in the region from 1800 to 670 cm^{-1} . These all show a strong characteristic absorption band at $1340 \pm 10 \text{ cm}^{-1}$ which is assigned to the asymmetrical stretching frequency of the BO_3 group.

Comparison of the infra-red and Raman spectra of trimethyl borate suggests the assignment of the 728 cm^{-1} Raman band to the symmetrical stretching mode. The non-coincidence of infra-red and Raman bands indicates a fairly high degree of symmetry with restriction of the rotation of the methyl groups round the B—O link. This contrasts with other data on the behaviour in the vapour where such rotation may occur.

I. INTRODUCTION

Although several investigators have reported on the Raman spectra of the esters of boric acid (Ananthkrishnan 1936 ; Joglekar and Thatte 1936 ; Milone 1936 ; Kahovec 1938, 1939) as far as we are aware, the infra-red spectra of this class of compounds have not been recorded. Kahovec showed that the original Raman lines recorded by Ananthkrishnan were substantially correct while those of Milone and Joglekar and Thatte were unreliable. He pointed out, however, that the assignments of Ananthkrishnan to the BO_3 group in the case of trimethyl borate, made on the basis of the pyramidal model (symmetry C_{3v}), required revision since evidence from other sources, for example the electron diffraction measurements of Bauer and Beach (1941), had shown that the BO_3 group was coplanar.

The infra-red spectra of these compounds would therefore be useful, not only by indicating the bands characteristic of the BO_3 group in the infra-red region, but also in assisting in the correct assignment of the Raman bands to this group. In this paper, therefore, data are presented on a representative series of borate esters in the region from 1800 to 670 cm^{-1} .

II. EXPERIMENTAL

The compounds examined were prepared by one of us (K.G.O'B.) by methods to be described elsewhere. Precautions in handling were necessary as the samples readily hydrolysed. After anhydrous fractionation the liquid samples were immediately sealed in glass tubes which had previously been baked out.

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Samples, which condensed as solids on distillation, were mulled with paraffin oil in a "dry box" and were then safe to handle. The spectra were run on liquid capillaries or pastes between rock-salt plates. By placing several drops on a plate and then sliding a second plate over this with a wiping motion, the thin hydrolysed layer which formed on the surface was effectively removed. That these precautions were sufficient was shown by the fact that in the spectra taken only small hydroxyl bands were revealed in the 3μ -region, and these on thick samples only. Such small contamination as may have occurred by the presence of hydrolysed products can have had only a very minor effect on the spectrograms.

TABLE 1A
THE INFRA-RED SPECTRA OF THE BORIC ACID ESTERS*

Trimethyl	Tri- <i>n</i> -propyl	Tri- <i>n</i> -butyl	Tri- <i>n</i> -amyl	Assignment
1484 (s)	1486 (m)	1483 (m)	1495 (m)	—CH ₂ — bending —CH ₂ — bending —CH ₃ bending B—O stretching
1417 (m)	1417 (s)	1417 (s)	1417 (s)	
1377 (s)	1354 (s)	1360 (ms)		
1348 (vs)	1334 (vs)	1336 (vs)	1340 (vs)	
	1298 (m)	1298 (ms)	1279 (m)	
	1280 (m)	1261 (m)	1243 (m)	
	1255 (m)	1232 (m)	1218 (w)	
1183, 1172 (m)				
1112, 1095 (vw)	1102 (vw)	1118 (w)	1119 (w)	C—O stretching
			1077 (m)	
1032 (s)	1072 (s)	1071 (s)	1056 (s)	
	1054 (m)	1031 (m)	1009 (m)	
	1016 (w), 997 (w)			
	973 (m)	969 (m)	987 (w)	
883 (w)	911, 895, 873 (w)	852 (vw)	893 (w), 843 (vw)	
815, 773 (w)	757 (w)	738 (w) *	775, 730 (w)	
	693 (w)	692 (w)	690 (mw)	
	665 (m)		670 (m)	

* See footnote to Table 1B.

The spectra were obtained on a Perkin-Elmer 12C single beam spectrometer with sodium chloride optics. Calibration was effected in the usual manner against the data of Oetjen, Kao, and Randall (1942).

III. DISCUSSION

The absorption bands recorded in the range 670 – 1800 cm^{-1} are presented in Table 1A, 1B; and the relationship of corresponding bands in different compounds is shown by means of a line graph in Figure 1.

By analogy with bonds similar to B—O and by an approximate calculation it would appear likely that the BO_3 group absorbs in the region between 1000 and 1500 cm^{-1} . In this region there occur also bands due to C—O stretching and C—H in-plane bending vibrations from which the B—O absorption must be differentiated. The C—O stretching frequency in the series studied is readily identified. In the esters of the primary alcohols it occurs close to 1060 cm^{-1}

except for the first member of the series, trimethyl borate, which is somewhat lower. As the degree of substitution of the carbon atom increases the band would be expected to move to higher frequencies (Colthup 1950) and in agreement with this we find the band at 1130 and 1124 cm^{-1} in the secondary alkyl esters and still higher at 1216 and 1217 cm^{-1} in the aromatic esters. The band position in tricyclohexyl borate (1062 cm^{-1}) is slightly low, but this may well be a steric effect.

TABLE 1B
INFRA-RED SPECTRA OF THE BORIC ACID ESTERS*

Tri-sec.-butyl	Tri-2-octyl	Triphenyl†	Tricresyl†	Tricyclohexyl†	Assignment
		1593 (s)	1615 (m)		Phenyl
			1598 (w)		
		1486 (s)	1511 (s)		Phenyl
1453 (m)	1456 (m)				
1423 (ms)	1419 (m)	1400 (s)	1413 (m)	1424 (m)	C—H bending
1396 (s)	1396 (s)			1398 (s)	
1374 (s)	1376 (ms)		1367 (s)	1361 (s)	
1330 (vs)	1331 (vs)	1350 (vs)	1345 (vs)	1331 (vs)	B—O stretching
1303 (m)			1303 (w)		
1271 (w)		1242 (w)	1257 (w)	1257 (w)	
1173 (w)	1198 (w)		1233 (w)	1238 (w)	
1131 (s)	1124 (s)	1217 (s)	1216 (s)	1062 (ms)	C—O
1114 (m)	1074 (m)	1166,	1171 (m)		
		1153 (w)	1103 (m)		
1032 (m)	1040 (w)	1071 (m)	1044 (w)		
994 (m)		1024 (mw)	1018 (w)	1028 (w)	
973 (w)	976 (w)			969 (m)	
914 (m)	937 (w)			892 (w)	
	863 (vw)	854 (w)	852 (w)		
833 (w)		836, 822 (m)			
779 (w)		767 (s)	821 (s)		Phenyl
			812 (s)		
			757 (m)		
	724 (w)	723 (m)	738 (w)		
			714, 707, 703 (w)		
		692 (ms)			Monosubstituted phenyl
	690 (mw)				

* The absorption bands of the borate esters in the infra-red region between 1800 and 670 cm^{-1} .

† The triphenyl, tricyclohexyl, and tricresyl borates were examined as solids, the remainder as liquid capillary films.

In the region between 1300 and 1500 cm^{-1} there appear several bands some of which must be due to hydrogen in-plane bending vibrations. A characteristic pattern of bands is discernible for the primary alkyl esters which differs from the secondary alkyl and aryl compounds. These we assign to the hydrogen bending modes.

Common to all the spectra, whether alkyl or aryl, is the presence of a very strong band at $1340 \pm 10 \text{ cm}^{-1}$. This band in fact, is the strongest in this region of the spectrum in every case and its intensity is such that capillary samples were necessary to prevent complete absorption at the peak. There seems little doubt that this is due to the B—O linkages in the molecule.

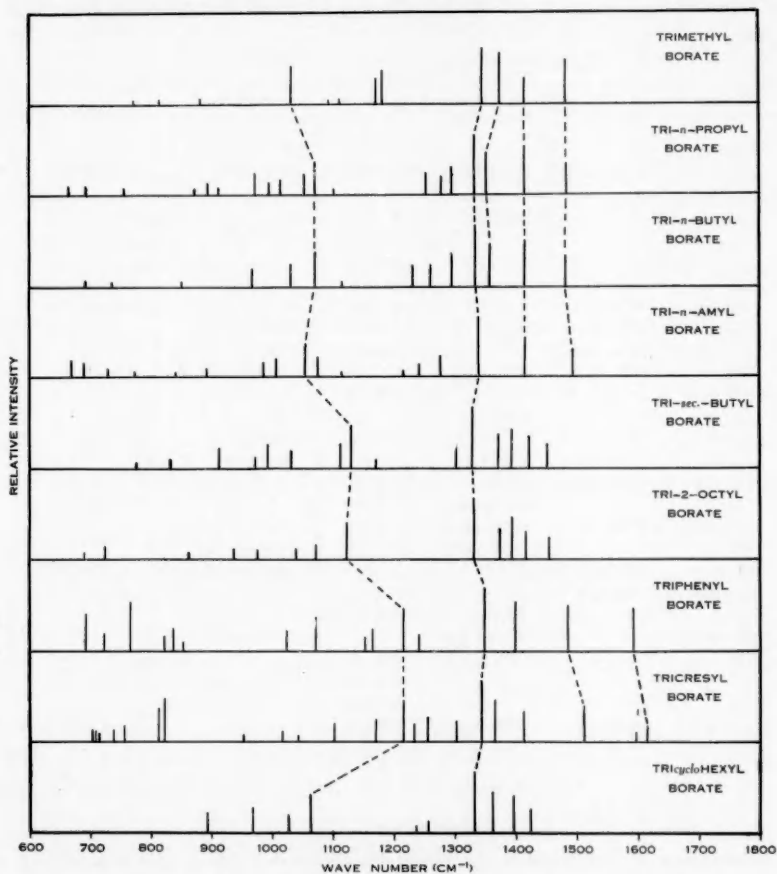


Fig. 1.—Correlation of absorption peaks of the borate esters in the region between 1800 and 670 cm^{-1} .

In support of this assignment we note that Bethell and Sheppard (1955) record a value of 1450 cm^{-1} for the B—O stretching frequency in crystalline boric acid.

The narrow range over which the band falls (20 cm^{-1}) contrasts with the spread of the C—O bands (nearly 200 cm^{-1}) which are considerably influenced by the substituent. This suggests a partial double bond character and is in

accord with the value of 1.40 for the bond order obtained by the application of Gordy's (1947) equation.

$$N = \frac{a}{R^2} + b,$$

where N is the bond order, a and b are constants, respectively 6.75 and -2.14 , and R is the interatomic distance, taken in this case from the electron diffraction data of Bauer and Beach (loc. cit.) as 1.38 Å.

In the case of the simplest member of the series, trimethyl borate, we can attempt an assignment of the infra-red and Raman bands using the planar XY_3 system as a model. The normal vibrations of such a system (symmetry D_{3h}) are shown in Figure 2. It seems clear that the strong polarized Raman line reported by Ananthkrishnan (loc. cit.) at 728 cm^{-1} is to be identified with the symmetric "breathing" frequency ν_1 , while the symmetrical stretching frequency ν_3 , which should be Raman inactive, gives rise to the strong infra-red

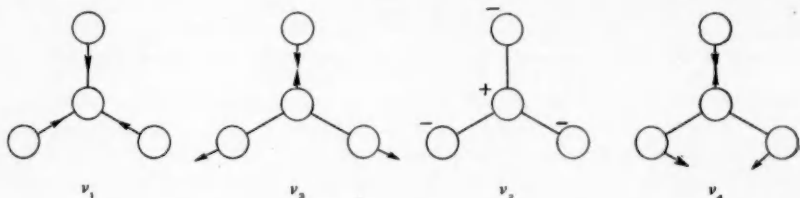


Fig. 2.—The normal vibrations of the planar XY_3 system.

absorption at 1348 cm^{-1} . On the other hand the assignment of ν_2 , which corresponds to a movement of the boron atom above and below the plane of the oxygen atoms, and of ν_4 , which involves a bending of the BO groups, is more difficult. These doubly degenerate vibrations should be both infra-red and Raman active and should give rise to Raman depolarized lines. The frequencies are apparently beyond the range of the present infra-red work but Ananthkrishnan reports Raman lines at 526 and 197 cm^{-1} (depolarized) and 320 cm^{-1} (polarized). While this would appear to indicate that 526 cm^{-1} (ν_2) and 197 cm^{-1} (ν_4) are the frequencies in question, the value of 197 cm^{-1} seems too low to be probable. The question would be resolved if the infra-red data to 40μ were available and it is hoped to obtain this information shortly by using a caesium bromide prism.

It might appear that the application of vibrational modes and selection rules characteristic of a simple XY_3 molecule, to a molecule as complex as trimethyl borate is a gross approximation. On the other hand the complete absence of the symmetrical stretching frequency ν_1 from the infra-red spectrum, together with the corresponding absence of the asymmetrical frequency ν_3 from the Raman spectrum, would indicate that a high degree of symmetry still exists despite the methyl groups. This suggests that the methyl groups are locked into a symmetrical configuration with respect to the BO_3 group in contradistinction to the vapour where electron diffraction data (Bauer and Beach

loc. cit.) indicate that rotation of the methyl group around the BO-axis is possible.

In the higher esters this degree of symmetry is presumably lost, as may be judged by the increase in the complexity of the spectra (both infra-red and Raman) compared to trimethyl borate and by the fact that the selection rules begin to break down. Thus, one finds recorded in the Raman spectra of the esters above methyl, the presence of weak bands near 1340 cm^{-1} corresponding to the infra-red active frequency ν_3 (Kahovec loc. cit.).

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HEATS OF MIXING OF ALCOHOL SOLUTIONS

By I. BROWN* and W. FOCK*

[Manuscript received March 21, 1955].

Summary

A calorimeter for the measurement of the heats of mixing of binary liquid systems at temperatures from 20 to 45 °C is described.

Heats of mixing have been measured for approximately equimolar mixtures of benzene+carbon tetrachloride at 25 °C, benzene+ethylene dichloride at 25 °C, acetone+chloroform at 25 °C, and ethanol+carbon tetrachloride at 45 °C. Measurements have been made at intervals over the whole composition range of the systems ethanol+2,2,4-trimethylpentane at 25 °C and ethanol+benzene at 45 °C.

I. INTRODUCTION

The accurate determination of heats of mixing at elevated temperatures was required for a study of the thermodynamic properties of binary mixtures of alcohols and polar liquids. Measurements become more difficult as the temperature is raised owing to the increased vapour pressure and the expansion of the liquids. Temperatures up to 45 °C were chosen so that the heats of mixing could be measured without undue difficulty.

For accurate measurements using reasonably small quantities of material, it is desirable to eliminate the latent heat effect due to evaporation and that due to a change in vapour composition on mixing. It is also necessary to keep exchange of heat between the calorimeter and its surroundings to a minimum. The bell type of apparatus used by Tompa (1952), the U tube type used by Scatchard *et al.* (1952) and Thacker and Rowlinson (1954), and the apparatus of Cheesman and Whitaker (1952) have been designed to overcome one or more of these difficulties. Adecock and McGlashan (1954) have recently described an apparatus of the bell type which gives accurate results over a wide range of temperatures and uses small quantities of liquid.

The apparatus described here is of the U tube type, using mercury to separate the liquids to be mixed and two expansion capillaries of the type used by Cheesman and Whitaker (1952) to prevent mixing of the vapour phases. Temperature changes are measured with a thermistor, and thermal insulation is provided by a high vacuum.

II. APPARATUS

The assembly of the apparatus is shown diagrammatically in Figure 1, the whole being installed in a constant temperature room held at 20 ± 0.2 °C. The mixing cell *A* is mounted on a pinion shaft *B*, which passes through a double

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Wilson seal in the back of a cast aluminium alloy vacuum box *C*, having a heavy brass cover *D*. The box is mounted in a thermostat bath *E* filled with high-flashpoint "Kerosene", which is maintained at the desired temperature to $\pm 0.005^\circ\text{C}$; fluctuations within the box itself are considerably less. The aluminium box is evacuated at *G* by a 4 in. diameter oil diffusion pump which reduces the pressure in the box to less than 0.05μ . All "Hycar" or "Neoprene" vacuum gaskets are rectangular in section and fitted into carefully lapped grooves. The cell contents are mixed and stirred by the oscillating mechanism *F* which consists of a synchronous motor driving a rack and pinion through a reduction gear and crank. The shaft is oscillated through an angle of 220° at a frequency of 4.5 c/min.

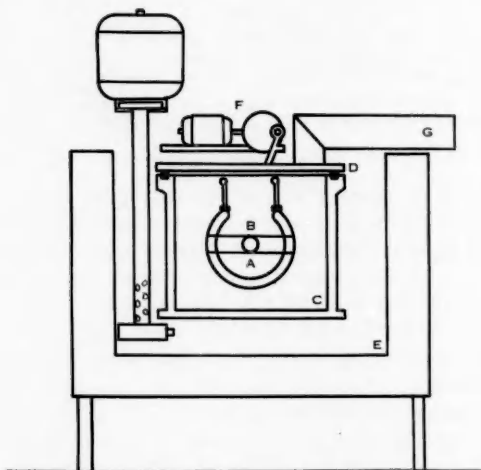


Fig. 1.—Assembly of apparatus.

The mixing cell is shown in Figure 2. It is made from 16 mm diameter stainless steel tube with screwed outlets welded to each end. These are closed by 1.0 mm internal diameter glass capillaries mounted in conical collars and attached by mild steel union nuts. A 0.75 mm "Teflon" gasket between the polished metal and glass surfaces provides a seal. These gaskets are sliced from a machined "Teflon" tube on a lathe by a razor, as striations in peeled "Teflon" sheet permit leakage into the vacuum system. The thermistor is mounted, just clear of the bottom, in a stainless steel pocket welded into the cell. A few drops of silicone oil in this pocket improve thermal conduction.

All protuberances are kept as small as possible and made of high thermal conductivity material to ensure rapid temperature equalization of the cell and its contents.

The lower half of the cell is coated with "Araldite" synthetic resin, over which the 12Ω heater is wound non-inductively from 116 cm of 0.25 mm silk-

covered manganin wire. A further coat of "Araldite" separates the heater from a layer of copper foil strip wound around it to improve the heat conduction into the cell.

The cell is mounted in a cradle of glass fibre sheet bonded with synthetic resin and is surrounded by a loose radiation shield of thin aluminium foil.

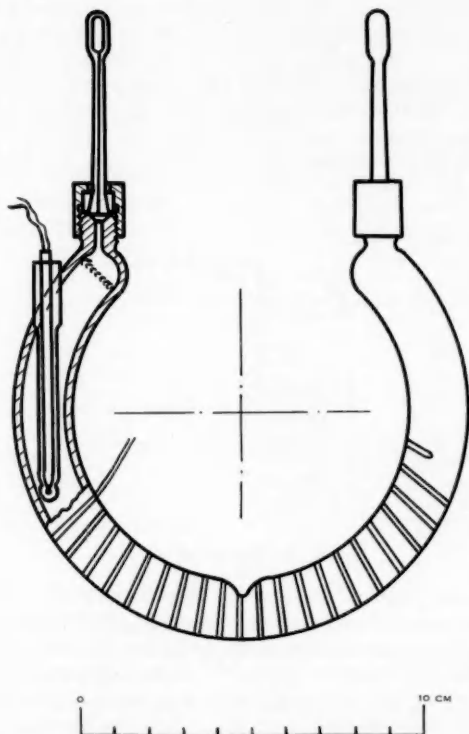


Fig. 2.—Mixing cell.

Flexible electrical leads connect the thermistor and heater to a six-pin connector under the vacuum box lid, whence connections to the external circuits are made through glass-metal seals soldered into the lid.

The thermistor used is a S.T.C. type F1512/300, having a resistance of $104,000\Omega$ at 25°C and $45,000\Omega$ at 45°C . The resistance measuring circuit consists of a Wheatstone bridge, one arm of which contains the thermistor, a $10,000\Omega$ decade box, and a microammeter in series. The current through this arm is preset to $20\mu\text{A}$ at balance by altering the voltage applied to the bridge, this low value is chosen to minimize the heating effect in the thermistor bead

while still giving sufficient sensitivity. The detector is a reflecting galvanometer with a sensitivity of $1500 \text{ mm}/\mu\text{A}$ at 1 m . Overall sensitivity is 1 to $2 \Omega/\text{mm}$.

The heater circuit is shown in Figure 3. Both the cell heater H and the dummy heater D are wound from 116 cm of 0.25 mm diameter manganin wire and have a resistance of 11.866Ω at 25°C , and 11.868Ω at 45°C . The dummy heater is mounted in the thermostat bath. A steady direct current is supplied by a lead-acid accumulator. The heater current is evaluated by measuring the potential across a calibrated standard 2Ω resistance R using a Tinsley portable potentiometer P . A double-pole, double-throw mercury switch S is used to substitute the cell heater for the dummy and also to start and stop an electronic interval timer T . The timer is comprised of six Eccles-Jordan trigger circuits, the last of which operates a mechanical indicator. The interval timer can measure intervals to $\pm 0.02 \text{ sec}$; it is operated from the power mains at a frequency of 50 c/s .

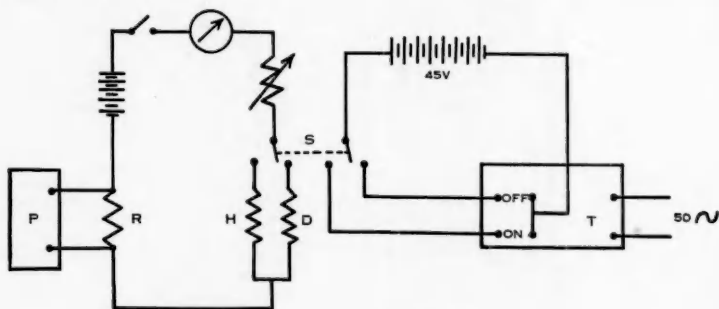


Fig. 3.—Heater circuit.

III. PURIFICATION OF LIQUIDS

The purification and physical properties of the ethanol, benzene, and carbon tetrachloride have been described previously (Brown and Smith 1954*a*, 1954*b*). Analar chloroform and ethylene dichloride were washed with dilute sodium carbonate solution and with water, and were then fractionally distilled. Analar acetone was fractionally distilled and the middle fraction dehydrated by the method of Thirion and Craven (1952).

A batch of 95 per cent. pure 2,2,4-trimethylpentane was shaken with concentrated sulphuric acid, washed with dilute sodium carbonate solution and water, and fractionally distilled.

The densities and refractive indices of the liquids used are shown in Table 1.

IV. EXPERIMENTAL PROCEDURE

The mixing cell is filled by means of a hypodermic syringe with a bent needle. A charge of 170 g of mercury is used for most experiments except those where large heats of mixing are encountered, when about twice this amount is used. The cell is weighed after the mercury and each component have been introduced. When working at elevated temperatures a calculated amount of

each component is removed after preliminary weighing to allow for thermal expansion and the cell is then reweighed. The weight of each component can be measured to ± 10 mg.

After filling, the cell is mounted on the pinion shaft in the vacuum box and all electrical connections are made. After allowing the cell to reach operating temperature (about 2 hr) the vacuum box is evacuated by the roughing pump and left overnight with a current of $20\mu\text{A}$ flowing through the thermistor circuit. The box is further evacuated using the diffusion pump, which after an hour reduces the pressure to below 0.05μ . A further period of 2 hr is allowed for thermistor stabilization; a current of from 0.1 to 0.2 A flowing in the dummy circuit allows the heater current to stabilize.

At the start of the run the bridge is balanced with about 5000Ω in series with the thermistor, further balancing being done by altering this series resistance. Readings are taken at 1 min intervals. At 5 min, the cell oscillating mechanism is set in motion, and further readings of the resistance are taken every minute.

TABLE I
PHYSICAL PROPERTIES OF COMPONENT LIQUIDS

Liquid	n_D^{25}	d_4^{25}
Ethanol	1.35929	0.78511
Benzene	1.49803	0.87359
Carbon tetrachloride ..	1.45734	1.58435
Chloroform	1.44329	1.48073
Ethylene dichloride ..	1.44228	1.24546
Acetone	1.35599	0.78494
2,2,4-Trimethylpentane ..	1.38908	0.68766

At 25 min, current is passed through the cell heater for a period of from $\frac{1}{2}$ to 3 min depending on the mixture, and resistance readings taken for a further 20 min. During the heating period the potential across the standard resistance is measured by the potentiometer.

When the cell is charged with pure liquids the mol fraction of the resulting mixture is in the range 0.4 to 0.6. To obtain mixtures with higher or lower mol fractions, one side of the cell is filled with a mixture whose heat of mixing is known from a previous run.

For systems with a negative heat of mixing two procedures have been used. The first is similar to that used normally. The second is done in two stages: the resistance change on mixing is determined first, and the cell allowed to regain its equilibrium temperature overnight; the oscillation is then continued and the resistance change on heating determined in the usual manner. The two methods showed no significant difference in their results.

V. CALCULATIONS

For a mixture with positive heat of mixing, Figure 4 records a typical set of measurements of resistance at different times.

To determine the resistance change on mixing, a point *D* is chosen 10 min after mixing commences, and the line *ED* extrapolated to intersect a vertical line through *B* at *C*. The resistance change on heating is found in a similar way by extrapolating to the vertical line corresponding to the cessation of the heat input. The temperatures corresponding to the points *B*, *C*, *E'*, and *F* were found from a calibration of the thermistor, and were used to determine the temperature changes on mixing and heating: *K* and *L* degrees respectively. The heat of mixing in absolute joules per g mol of mixture is then given by:

$$H^M = KI^2R\theta/LM,$$

where *I* is the heater current and *R* its resistance, θ the duration of current flow through the heater, and *M* is the total number of moles of the mixture.

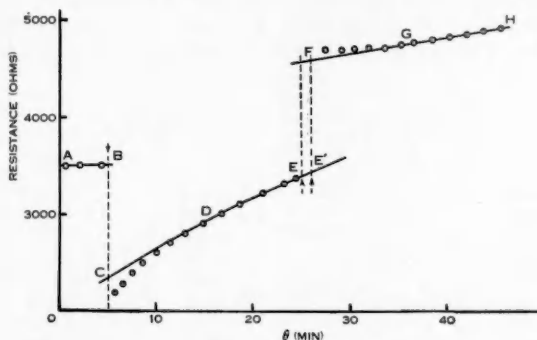


Fig. 4.—Resistance-time curve.

VI. RESULTS

Measurements of the heat of mixing of approximately equimolar mixtures of three systems were made for comparison with published data. To enable this to be done at the experimental mol fractions, graphs of published values of H^M/x_1x_2 were drawn and the values read off at the required concentrations. In all cases x_1 represents the mol fraction of the first mentioned component.

(a) Benzene and Carbon Tetrachloride

Author	Temperature (°C)	H^M (J/mol) at $x_1 =$		
		0.567	0.576	0.580
Present work	25.0	107	110	110
Cheesman and Whitaker (1952)	24.7	106	106	106
Hirobe (1926)	25.0	105	105	105
Boissonas and Cruchard (1944)	25.0	108	108	108

The temperature variation of the heats of mixing of this system is illustrated by these results and those of Cheesman and Whitaker (1952) at 17.8 °C, Schulze (1951) at 15 °C, and Scatchard, Wood, and Moehel (1940) at 55 °C. In comparison with these, the results of Vold (1937) at 25 °C are low, while those of Baud (1915) at 15 to 20 °C and Schmidt (1926) at 18 °C are high.

(b) *Benzene and Ethylene Dichloride*

Author	Temperature (°C)	H^M (J/mol) at $x_1 =$	
		0.525	0.526
Present work	25.0	63.3	61.6
Cheesman and Whitaker (1952)	24.7	60.1	60.1
Korvezee, Ruiter, and Stuyts (1953)	24.7	60.5	60.5

(c) *Acetone and Chloroform*

Author	Temperature (°C)	H^M (J/mol) at $x_1 =$	
		0.467	0.474
Present work	25.0	-2000	-1965
Hirobe (1926)	25.0	-1955	-1950
Schmidt (1926)	14.0	-2280	-2280

The values of Carroll and Mathews (1924) at 60 °C when plotted as H^M/x_1x_2 are not self-consistent.

(d) *Ethanol and Carbon Tetrachloride at 45.0 °C*

x_1	H^M (J/mol)
0.537	511*
0.550	480
0.605	368*
0.671	273

* Previously reported: *Disc. Faraday Soc.*

15: 142 (1953).



(e) *Ethanol and 2,2,4-Trimethylpentane at 25.0 °C*

x_1	$H^M(a)$ (J/mol)	$H^M(b)$ (J/mol)
0.117	537	887
0.233	645	1004
0.425	661	975
0.703	491	690
0.783	405	544
0.869	289	355
0.950	134	113

$H^M(a)$ are the values obtained in this work, while those shown in comparison are calculated from the excess free energies of mixing obtained by Kretschmer and Wiebe (1948).

(f) *Ethanol and Benzene at 45.0 °C*

x_1	H^M (J/mol)	x_1	H^M (J/mol)
0.130	1047	0.639	920
0.189	1231	0.651	899
0.276	1298	0.653	861
0.330	1320	0.857	390
0.547	1096	0.940	173
0.549	1098		

The values of published data are compared below at 0.5 mol fraction.

Author	Temperature (°C)	H^M (J/mol)
Present work	45	1170
Pahlke (1935)	20	760
Perrakis (1925)	20	675
Violla (1914)	20	470
Winkelmann (1873)	15	465
Winkelmann (1873)	5	410
Winkelmann (1873)	0	390

The results of Carroll and Mathews are not self-consistent; those of Pahlke and Perrakis at 20 °C, which cover different ranges of concentration, appear to be in reasonable agreement.

VII. ERRORS

The maximum errors in the values of the heats of mixing due to errors in the measured quantities have been determined. For the systems *a*, *b*, *c*, and *d* the errors are approximately 3 per cent., and for the others the error is 2 per cent. at the middle of the concentration range, and 3 per cent. at the extremities. The major contribution to the error is the uncertainty in extrapolation of the resistance-time curves (about two-thirds of the error); the error due to weighing is the next most important.

VIII. CONCLUSION

The apparatus described is capable of yielding useful heat of mixing data at temperatures up to 45 °C. Increased accuracy could probably be obtained by the simultaneous mixing and addition of heat as used by Adcock and McGlashan (1954). The accuracy is far greater than that which could be obtained from calculations based on free energy data at two adjacent temperatures.

IX. ACKNOWLEDGMENTS

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ON THE LOW-TEMPERATURE OXIDATION OF *iso*BUTANE AND PROPYLENE

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[Manuscript received March 29, 1955]

Summary

The low-temperature oxidation of *isobutane* and propylene has been studied by interrupting the reaction by withdrawing the partly reacted mixture from the reaction vessel. After treatment designed to destroy peroxides the mixture was returned to the reaction vessel. The results show that the termination of the induction period is due to the accumulation of an active intermediate or intermediates in the gas phase. In both systems these intermediates are probably not alkyl hydroperoxides.

Changes in the surface of the reaction vessel brought about by processes occurring in the early stages of the reaction do not contribute to the termination of the induction period.

I. INTRODUCTION

The reaction between hydrocarbon vapours and oxygen is characterized by an induction period of little or no pressure change, followed by a period of accelerating increase in pressure. Depending upon the actual conditions, the reaction may proceed to cool flame or ignition, or the rate may merely pass through a maximum and decrease as the reagents are spent. Hydrocarbons containing three or more carbon atoms may show a different mechanism at high temperatures from that observed at low temperatures (see Townend 1937). The two modes of oxidation are generally considered to be "degenerate branching chain reactions", that is, chain reactions in which branching takes place through a relatively stable intermediate (Semenov 1935). However, despite a great number of investigations, there is still little agreement regarding the details of oxidation mechanisms, and a particular subject of discussion is the identity of the active intermediate responsible for degenerate branching, although for the high-temperature mechanism the evidence points to formaldehyde (Bailey and Norrish 1952). Organic peroxides, particularly hydroperoxides (Ubbelohde 1935; Walsh 1946; Hinshelwood 1947) and aldehydes (Norrish 1948, 1951; Knox and Norrish 1954), have both been postulated as the important intermediates in the low-temperature reaction.

The peroxide theory of the low-temperature oxidation of hydrocarbons has several attractive features. Most products of oxidation of hydrocarbons contain separate oxygen atoms. The separation of the atoms of molecular oxygen can easily be imagined to take place through the splitting of an intermediate peroxide at the O—O bond. Also, oxidation reactions are far more sensitive to the structure of the hydrocarbon than are decomposition reactions. This has been

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attributed to the various effects of different alkyl groups on the strength of the O—O bond in the peroxide molecule (Hinshelwood 1948 ; Walsh 1948). However, for propane, it has been claimed that there is no evidence for the presence of hydroperoxides among the oxidation products (Knox and Norrish 1954), and Shtern and Polyak (1949), Polyak and Shtern (1953), and Pease and Munro (1934) claim that removal of peroxides during the oxidation of propylene and propane respectively has no effect upon the subsequent course of the reaction.

The present paper describes a series of experiments designed to determine the role played by peroxides and other compounds in the low-temperature oxidation of hydrocarbons. *iso*Butane and propylene have been used in the experiments. The oxidation of *isobutane* has been studied by Batten, Gardner, and Ridge (1955), and that of propylene by Mulcahy and Ridge (1953a). On oxidation both these hydrocarbons yield higher aldehydes and peroxides. There is evidence that *tert*.-butyl hydroperoxide, or at least the corresponding peroxy radical, plays a part in the oxidation of *isobutane* (Batten, Gardner, and Ridge 1955).

II. EXPERIMENTAL

(a) General

The apparatus for observing the reactions and the technique for obtaining reproducible induction periods have already been described (Mulcahy and Ridge 1953a).

The induction period was defined as the time required for the rate of pressure increase to reach 0.5 mm/min.

Two sets of experiments were carried out as follows :

- (i) Preliminary experiments in which "possible" reaction products were added to *isobutane*-oxygen mixtures at 291 °C.
- (ii) Experiments in which the reaction of oxygen with either *isobutane* or propylene was interrupted by withdrawing the mixture from the reaction vessel and then returning it after treatment designed to destroy peroxides.

(b) Procedure in Experiments involving the Interruption of the Reaction

It has been observed in several laboratories and confirmed by the authors that peroxides in the vapour phase are destroyed if they come in contact with mercury. This fact has been used in the second set of experiments. The apparatus used is shown in Figure 1, and consisted of a narrow trap *A*, a Toepler pump *B* (volume 250 c.c.), connected to a storage vessel *C* (volume 550 c.c.), through a mercury-sealed float-valve *D*. The storage vessel could be connected to the reaction vessel and the analysis system. When filled, the storage vessel was maintained in darkness.

The actual experiments were carried out as follows : The reactants were admitted to the reaction vessel in the usual way. The mixture was then immediately pumped into the storage vessel and transferred back to the reaction vessel again, with as little delay as possible. This was done as a control for possible contamination of the Toepler pump and storage vessel by active intermediates from previous experiments. At a preselected stage in the reaction the

mixture was again transferred to the storage vessel. The reaction vessel could then be reconnected to the pumping system. The partly reacted mixture could either be admitted to the analysis system, or readmitted to the reaction vessel as desired. In some experiments the sides of the trap were covered with globules of mercury, but no further effect was produced in this way. Preliminary experiments showed that mercury vapour included in the reaction mixture on passing through the Toepler pump had no significant effect upon the reaction.

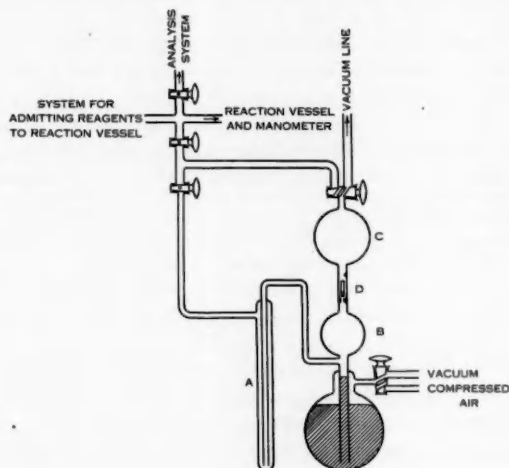


Fig. 1.—The apparatus used for interrupting the reaction and storing the partly reacted mixture.

(c) Materials

The acetone, acetaldehyde, and formic and acetic acids used were reagent grade materials purified by distillation. The formaldehyde was prepared by heating dry paraformaldehyde in the evacuated sampling vessel. The water was twice distilled. The propylene (Mulcahy and Ridge 1953*a*), oxygen, isobutane, and *tert*-butyl hydroperoxide (Batten, Gardner, and Ridge 1955) were prepared as described elsewhere.

(d) Determination of Peroxides

Peroxides were determined iodometrically. The sample was taken at -80°C as described previously (Mulcahy and Ridge 1953*a*). While warming to room temperature the reaction products were shaken with 15 ml of freshly purified acetic anhydride (Fieser 1941) and 0.5 g potassium iodide in the sampling vessel. After 5 min, 50 ml water and 25 ml purified carbon tetrachloride were added and the liberated iodine titrated with 0.01N thiosulphate, with constant shaking (see Batten 1955). Under these conditions the starch end-point was stable for several hours.

III. RESULTS AND DISCUSSION

(a) Effects of Compounds Added to isoButane-Oxygen Mixtures

Investigation of the low-temperature oxidation of *isobutane* (Batten, Gardner, and Ridge 1955) and propylene (Mulcahy and Ridge 1953a) has shown that, whereas some products accumulate continuously throughout the reaction, certain others (e.g. higher aldehydes, peroxides, and, to a lesser extent, formaldehyde) increase in concentration to a maximum coincident with the maximum rate of pressure rise, after which they decrease. It seems likely that the agent of degenerate branching is one of the latter group.

Table 1 shows the effects on the induction period and maximum rate of pressure change of adding acetone, acetaldehyde, acetic acid, formaldehyde, formic acid, *tert.*-butyl hydroperoxide, and water to 80 mm *isobutane* + 350 mm oxygen at 291 °C. (In all cases the reactants were added in the order: (i) hydrocarbon, (ii) additive, (iii) oxygen, except in the case of *tert.*-butyl hydroperoxide which was premixed with the oxygen.)

The added compounds may be grouped into the following two classes according to their effects: (1) Inhibitors: formaldehyde, formic acid, and water (which, however, slightly increases the maximum rate of pressure change); (2) accelerators: acetaldehyde, *tert.*-butyl hydroperoxide, acetone, and acetic acid.

The inhibiting effect of formaldehyde has been observed in low-temperature oxidations in other systems (Cullis and Hinshelwood 1947; Chamberlain and Walsh 1949; Downs and Walsh 1949). The opposite effect for the induction period in the oxidation of propylene was observed by Mulcahy and Ridge (1953a). We have confirmed this in a separate set of experiments. Likewise formic acid acts as an inhibitor for *isobutane* but as an accelerator for propylene. On the other hand, the effect of acetaldehyde is the same here as in the propylene-oxygen system.

Both acetaldehyde and *tert.*-butyl hydroperoxide were found to be strong accelerators, 1 mm pressure of each of these compounds reducing the induction period to less than half its original value. Batten, Gardner, and Ridge have shown that in the system 80 mm *isobutane* and 350 mm oxygen at 291 °C, the partial pressure of higher aldehydes is slight at the end of the induction period, but at the maximum rate reaches 4 mm. This concentration of aldehyde added to the system as acetaldehyde almost eliminates the induction period (see Table 1).

Despite the sensitivity of the induction period, the maximum rate was comparatively insensitive to the compounds added. For additions of up to 12 mm formaldehyde the variations were within the experimental error. This differs from the results for propylene (Mulcahy and Ridge 1953a). With acetaldehyde the maximum rate of pressure rise was affected only when such quantities were added that the induction period was almost eliminated. The quantities of *tert.*-butyl hydroperoxide added were without effect upon the maximum rate.

The difference in the effects of some substances from one system to another points to the individuality of each hydrocarbon-oxygen system. The magnitude

of the effects of the various "possible products" indicates that the accumulations of several substances may contribute to the termination of the induction period.

TABLE I
EFFECTS OF ADDITIONS OF VARIOUS COMPOUNDS ON THE INDUCTION PERIOD AND MAXIMUM RATE OF 80 MM *isobutane* + 350 MM OXYGEN AT 291 °C

Compound	Amount Added (mm)	Induction Period, θ (min)	Maximum Rate, ρ_{\max} (mm/min)	Remarks
Formaldehyde ..	0	28.5	17.0	Inhibits during induction period. Maximum rate unaffected
	0	27.5	—	
	2.1	35.5	17.8	
	5.0	43.5	16.6	
	12.0	53.0	16.5	
Formic acid ..	0	33.0	14.0	Inhibits during induction period and at maximum rate
	5	93.5	9.0*	
	0	33.0	10.5	
	8.7	107.5	9.0	
	0	37.5	8.0	
	3.0	39.0	6.6	
	4.8	59.0	6.5	
Acetaldehyde ..	0	23.5	18.5	Strong accelerator during induction period. Maximum rate not affected until induction period almost eliminated
	1.0	10.5	18.0	
	1.9	2.5	19.7	
	3.2	3.0	—	
	3.9	1.0	23.2	
	10.0	0	Explosion	
<i>tert.</i> -Butyl hydroperoxide	0	44	c. 10-11	Strong accelerator during induction period. Maximum rate unaffected
	1.0	15	10.5	
	1.0	21	—	
	2.0	4.5	10.8	
Acetone ..	0	24.5	17.0	Weak accelerator
	3.2	20.0	18.0	
	6.0	19.5	19.5	
	10.5	16.0	20.5	
	15.0	14.5	22.0	
Acetic acid ..	0	30.0	9.2	Weak accelerator
	3.8	26.0	9.6	
	8.0	14.0	11.0	
Water	0	37.5	6.8	Weak inhibitor during induction period; slight accelerator at maximum rate
	1.8	37.0	7.8	
	7.3	42.0	9.0	

* Formic acid added first.

(b) Contribution of Peroxides to the Termination of the Induction Period

Table 2 shows the effect of destruction of peroxide on the reaction in the systems 80 mm isobutane+350 mm oxygen (mixture A), and 200 mm

TABLE 2

EFFECT OF DESTRUCTION OF PEROXIDE ON REACTION BETWEEN isobUTANE AND OXYGEN AT 291 °C

Mix A: 80 mm isobutane+350 mm oxygen; mix B: 200 mm isobutane+100 mm oxygen

Mixture	Induction Period, θ (min)	Stage when Reaction Interrupted (min)	Time in Storage Vessel (min)	Induction Period on Return to Reaction Vessel (min)	Total Peroxide Content at Withdrawal (mm)	Total Peroxide Content after Stay in Storage Vessel (mm)
{ A A	23.0	$\theta+1.5$	23.5*	0.5	} 0.14	Nil
	24.0	$\theta+1.5$	25.0*	<0.5		
A	20.5	$\theta+2.0$	6.0	—	>0.14	Nil
B	28.0	$\theta+2.0$	30.5*	<0.5	0.19	Nil
B	32.5	$\theta+6.5$	26.0*	<0.5	1.9	0.18; 0.11

* Reaction vessel connected to diffusion pump for 15 min while mixture in storage vessel.

isobutane+100 mm oxygen (mixture B); Table 3 shows similar results for the system 80 mm propylene+350 mm oxygen. All experiments were carried out at 291 °C.

TABLE 3

EFFECT OF INTERRUPTION OF REACTION BETWEEN 80 MM PROPYLENE AND 350 MM OXYGEN AT 291 °C ON PEROXIDE CONTENT AND THE SUBSEQUENT REACTION

Induction Period, θ (min)	Stage when Reaction Interrupted (min)	Time in Storage Vessel (min)	Induction Period on Return to Reaction Vessel (min)	Peroxide Content at Withdrawal (mm)	Peroxide Content after Stay in Storage Vessel (mm)
51.5	$\theta+1.5$	24.5*	<0.5	} <0.19	<0.0 ₄
21.0	$\theta+1.0$	27.0*	<0.5		<0.0 ₄
35.5	$\theta+1.0$	58.5†	0.5		<0.0 ₄
32.0	$\theta+1.5$	90	—		<0.0 ₄
37.5	$\theta+0.5$	2 days‡	<0.5		<0.0 ₄
38.5	$\theta+0.5$	3 days‡	<0.5		<0.0 ₄
23.0	$\theta+0.5$	4 days‡	<0.5		<0.0 ₄

* Reaction vessel connected to diffusion pump for 15 min while mixture in storage vessel.

† Reaction vessel connected to diffusion pump for 45 min while mixture in storage vessel.

‡ Reaction vessel connected to diffusion pump for 20 min while mixture in storage vessel.

These results show that transferring the partly reacted mixture to the storage vessel has in all cases brought about a sharp decrease in the peroxide content.

*iso*Butane mixtures withdrawn 1.5 to 2 min after the end of the induction period (of length 6 min) were found to contain no peroxide after storage (see Table 2). In the case in which the mixture was withdrawn at $\theta + 6.5$ min the peroxide was not completely destroyed by the treatment but was reduced to one-tenth of its previous value. When the stored reaction mixtures were returned to the reaction vessel, reaction was resumed with an induction period of not greater than 0.5 min and continued much as though the interruption had not occurred. These results indicate that peroxides as detected by this method of analysis (alkyl hydroperoxides among others) are not responsible for the termination of the induction period in *isobutane*-oxygen mixtures.*

The propylene-oxygen mixtures show the same general pattern, except that peroxide was never completely destroyed, even when the mixture was let stand 4 days in the storage vessel. This is contrary to the results of Polyak and Shtern (1953) who carried out some similar experiments with propylene, but found a complete destruction of peroxide.† However, the smallness of the induction period when the treated mixture was returned to the reaction vessel, together with the marked reduction in the peroxide content on treatment, and the magnitude of the effect of *tert.*-butyl hydroperoxide in the *isobutane*-oxygen system make it unlikely that peroxides alone are responsible for the termination of the induction period in this case also. Moreover, if acetaldehyde in amount corresponding to the content of higher aldehyde at the maximum rate of pressure rise is added initially to the system, the induction period is eliminated (Mulcahy and Ridge 1953a).

(c) *Effect of Changes in Activity of the Surface during the Induction Period*

While the reaction mixture was held in the storage vessel, the reaction vessel was reconnected to the pumping system and restored to approximately its condition before the reagents were admitted. Nevertheless, mixtures withdrawn after the induction period reacted within 30 sec on return to the reaction vessel, regardless of the length of the intermediate pumping. These results show clearly that once the agent of degenerate branching is formed in sufficient quantity to initiate the reaction producing the pressure rise, the reaction proceeds regardless of the condition of the surface. This is in accord with the view of Batten, Gardner, and Ridge (1955) that the reaction during the induction period is surface inhibited, the end of the induction period marking a transition to a mechanism in which surface effects are much less important. However, these results show (contrary to previous suggestions, e.g. Mulcahy and Ridge 1953b) that the induction period is not simply a period during which the inhibitor is destroyed (i.e. the surface becomes poisoned), since it is found that once the agent of degenerate branching has reached an appropriate concentration, cleaning the surface by pumping produces no further induction period.

* Peroxides are detected before the end of induction period by the iodometric method (see Mulcahy and Ridge 1953a; Batten, Gardner, and Ridge 1955).

† Polyak and Shtern do not state their method of analysis, and it is possible that the authors' method reveals peroxides not detected by them.

IV. CONCLUSION

There is evidence that alkyl hydroperoxides occur during the oxidation of isobutane (Batten, Gardner, and Ridge 1955). However, the results of these experiments demonstrate clearly that, whether peroxides play an important part in the oxidation of hydrocarbons or not, the termination of the induction period is due to the accumulation in the gas phase of an active intermediate (the agent of degenerate branching). In the systems isobutane-oxygen and propylene-oxygen the active intermediate is probably not an alkyl hydroperoxide.

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SYNTHETIC ANTISPASMODICS

I. SOME 1,1-DIARYL-3-(4'-METHYL-1'-PIPERAZINO)-1-PROPENES

By J. CYMERMAN-CRAIG* and R. J. HARRISSON*

[Manuscript received February 4, 1955]

Summary

The Mannich bases obtained by reaction of 1-methylpiperazine and formaldehyde with acetophenone and 2-acetylthiophen respectively have been condensed with phenyl- and α -thienylmagnesium bromide, giving the 1,1-diphenyl, 1,1-di- α -thienyl, and 1-phenyl-1- α -thienyl-3-(4'-methyl-1'-piperazino)propan-1-ols. These have been dehydrated to the corresponding 1-propenes. Both the propanols and the propenes exhibit antispasmodic activity.

I. INTRODUCTION

A number of *N*-substituted 3-amino-1,1-diphenylpropan-1-ols (I; R=Ph) and prop-1-enes (II; R=Ph) (Adamson 1949) possessed moderate atropine-like properties (White, Green, and Hudson 1951), and the related 3-amino-1,1-dithienylpropan-1-ols (I; R= α -thienyl) and prop-1-enes (II; R= α -thienyl) (Adamson 1950) also showed neurotropic spasmolytic activity (Adamson and Green 1950; Green 1953). The considerable effect of the nature of the dialkyl-amino group on activity is known (Adamson 1951; Green 1953). No substances of this type containing a piperazino-substituent as the basic group had previously been prepared, and in view of the known low toxicity of piperazine compounds (cf. Hewitt *et al.* 1947) and of the development of the antihistaminic 4-*p*-chlorobenzhydryl-1-methylpiperazine ("Chloreyclizine") (Baltzly *et al.* 1949; Hamlin *et al.* 1949) the preparation of the corresponding 4-methyl-1-piperazino compounds (III and IV) was deemed of interest.

Mannich reaction of 4-methylpiperazine dihydrochloride, paraformaldehyde, and 2-acetylthiophen and acetophenone respectively, gave the basic ketones (V; R=Ph and V; R= α -thienyl), showing light absorption identical with the parent ketones (Table 1). Attempted distillation of V (R= α -thienyl) at 2 mm resulted in considerable fission (cf. Mannich and Heilner 1922; Mannich and Honig 1927) to α -thienyl vinyl ketone, identified as 2-thienylpyrazoline, previously prepared by Harradence and Lions (1938). Both Mannich bases could however be distilled unchanged at 0.05 mm.

Grignard reaction of V (R= α -thienyl) with 2-thienylmagnesium bromide gave the carbinol (III; R³=R⁴= α -thienyl), dehydrated by excess of hydrogen chloride to the propene (IV; R³=R⁴= α -thienyl), the dihydrochloride of which was dimorphous, and showed ultraviolet absorption maxima at 2640 and 2870 Å (Table 1).

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Because of the relative instability of the free Mannich bases, a Grignard reaction using the dihydrochloride of (V; R=Ph) with excess of phenylmagnesium bromide was carried out. Distillation at 0.01 mm gave the desired

TABLE I
ULTRAVIOLET LIGHT ABSORPTION⁽¹⁾

Compound ⁽²⁾	$\lambda_{\text{max.}}$ (Å)	$\epsilon_{\text{max.}}$
V; R= α -thienyl	2600	8650
	2850	6000
2-Acetylthiophen ⁽³⁾	2600	7800
	2850	5600
V; R=Ph	2430	11500
	2800	1000
Acetophenone ⁽⁴⁾	2440	15850
	2780	1000
III; R ³ =R ⁴ =Ph	2460*	1300
1,1-Diphenylethanol ⁽⁵⁾	2570*	350
IV; R ³ =R ⁴ =Ph	2520*	11400
1,1-Diphenylprop-1-ene ⁽⁵⁾	2510	12000
IV; R ³ =R ⁴ = α -thienyl	2640	13500
	2870	13500
IV; R ³ =Ph; R ⁴ = α -thienyl }	2600	11200
(isomer A)	2850	8800
VI; R=Ph ⁽⁶⁾	2580	11500
1-Phenylprop-1-ene ⁽⁷⁾	2490	14700
	2840	1000
IV; R ³ =Ph; R ⁴ = α -thienyl }	2600†	8800
(isomer B)	2850	11300
VI; R= α -thienyl ⁽⁶⁾	2860	13000
2-Vinylthiophen ⁽⁶⁾	2760	11000

⁽¹⁾ Determined in 95% alcoholic solution using a Beckman ultraviolet spectrophotometer, model DU. ⁽²⁾ All bases were used as their dihydrochlorides.

⁽³⁾ Szmant and Basso (1951). ⁽⁴⁾ Gillam and Stern (1954). ⁽⁵⁾ Ramart-Lucas and Hoch (1935). ⁽⁶⁾ Jackman *et al.* (1949). ⁽⁷⁾ Campbell *et al.* (1947). ⁽⁸⁾ Friedel and Orchin (1951).

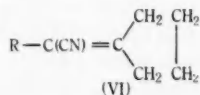
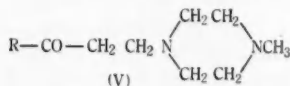
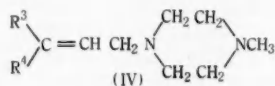
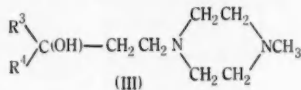
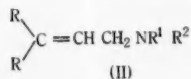
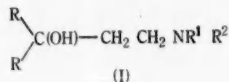
* Intense end-absorption.

† Inflection.

carbinol (III; R³=R⁴=Ph) showing only low-intensity absorption analogous to the related 1,1-diphenylethanol. The salts of this carbinol dehydrated on attempted recrystallization, giving the propene (IV; R³=R⁴=Ph), also obtained when excess of acid was used to decompose the Grignard reaction mixture.

The propene exhibited intense light absorption identical with 1,1-diphenylprop-1-ene (Table 1).

The mixed propanol (III; $R^3=Ph$; $R^4=\alpha$ -thienyl) was obtained from phenylmagnesium bromide and the dihydrochloride of V ($R=\alpha$ -thienyl). Distillation afforded equal amounts of the required carbinol (the salts of which dehydrated on recrystallization) and the corresponding propene (IV; $R^3=Ph$; $R^4=\alpha$ -thienyl). The salts of this propene appeared to be a mixture of isomers;



partition chromatography of the base on paper using aqueous acetic acid-butanol as the two phases showed separation into two substances, and fractional crystallization of the base from light petroleum gave a low-melting solid *A* and an oil *B*, both of which readily decolourized bromine. These gave two distinct series of isomeric salts showing small but definite m.p. depression on admixture. They differed markedly in their ultraviolet absorption spectra, and were thus the expected geometrical isomers.

The salts from base *A* gave the spectrum of 1-phenylprop-1-ene and of α -cyclopentylidenephénylacetonitrile (VI; $R=Ph$), while those obtained from base *B* showed light absorption analogous to 2-vinylthiophene and α -cyclopentylidene-2-thienylacetonitrile (VI; $R=\alpha$ -thienyl) (Table 1). The existence of geometrical isomers has been reported for 1-*p*-chlorophenyl-1- α -pyridyl-3-pyrrolidinoprop-1-ene (Adamson *et al.* 1951) where separation was achieved by crystallization of the oxalates.

In preliminary tests (for which we are indebted to Professor R. H. Thorp and Mr. R. Ladd of the Pharmacology Department of this University) on isolated guinea-pig ileum against spasms induced by barium chloride and carbachol using papaverine and atropine as standards, all compounds exhibited spasmolytic activity. Relative potencies are quoted on a molar basis in Table 2, which also gives the acute toxicities (LD_{50} , intravenous in mice). Compound IV ($R^3=R^4=\alpha$ -thienyl) was devoid of analgesic activity relative to morphine when tested in rats, in agreement with Green's (1953) findings of low analgesic activity in the 3-amino-1,1-dithienylpropenes (II; $R=\alpha$ -thienyl).

TABLE 2
SPASMOLYTIC ACTIVITIES

Compound	Relative Potency (M)		LD_{50} (mg/kg)
	Musculotropic	Neurotropic	
III; $R^3=R^4=\alpha$ -thienyl ..	10*	0.02	75
III; $R^3=R^4=Ph$	0.6	—	—
III; $R^3=\alpha$ -thienyl .. $R^4=Ph$	0.8	—	—
IV; $R^3=R^4=\alpha$ -thienyl ..	1.0	—	30
IV; $R^3=R^4=Ph$	6*	0.2	25
IV; $R^3=\alpha$ -thienyl $R^4=Ph$	1.0	—	—
Atropine	—	1.0	—
Papaverine	1.0	—	30

* Spasm of the guinea-pig ileum was induced with posterior pituitary extract.

II. EXPERIMENTAL

Analyses are by (the late) Mrs. E. Bielski, University of Sydney, and Dr. K. W. Zimmermann, C.S.I.R.O. Microanalytical Laboratory.

(a) *3-(4'-Methyl-1'-piperazino)-1- α -thienylpropan-1-one*.—A solution of 1-methylpiperazine dihydrochloride (7.65 g; 0.045 mol) and paraformaldehyde (2 g; 0.06 mol) in ethanol (35 ml) was heated under reflux and 2-acetylthiophen (6.8 g; 0.054 mol) in ethanol (15 ml) added dropwise. After a further 2 hr refluxing, the solution was concentrated *in vacuo* and on cooling 9.2 g (66% yield) of the Mannich base dihydrochloride separated, crystallizing from methanol in long needles, m.p. 222 °C (Found: N, 8.6; Cl, 22.4; S, 10.1%. Calc. for $C_{12}H_{18}ON_2S \cdot 2HCl$: N, 9.0; Cl, 22.7; S, 10.3%). The dipicrate crystallized from 2-ethoxyethanol in needles, m.p. 256 °C (Found: N, 16.2%. Calc. for $C_{12}H_{18}ON_2S \cdot 2C_4H_9O_2N_2$: N, 16.1%).

(b) *Attempted Distillation of Mannich Base*.—Attempted distillation of the base from a run identical with that described above gave three fractions: (1) b.p. up to 77 °C/2 mm (2 g), n_D^{14} 1.5187; (2) b.p. 77–85 °C/2 mm (3.7 g), n_D^{14} 1.5461; (3) b.p. 95–105 °C/2 mm (2 g), n_D^{14} 1.5515. Fractions 2 and 3, dissolved in ether and treated with dry hydrogen chloride, gave the Mannich base dihydrochloride (2.5 g), m.p. and mixed m.p. 222 °C. The combined ethereal filtrate and fraction 1, on treatment with phenylhydrazine, gave 2-thienylpyrazoline (5 g), crystallizing from 95% ethanol in yellow needles, m.p. 102.5 °C. Harradence and Lions (1938) give m.p. 103 °C.

(c) *1,1-Di- α -thienyl-3-(4'-methyl-1'-piperazino)propan-1-ol*.—To an ice-cold solution of 2-thienylmagnesium bromide, from 2-bromothiophen (10 g; 0.06 mol) and magnesium (1.45 g; 0.06 mol) in ether (25 ml), was added a solution of the Mannich base (V; R = α -thienyl) (4.8 g; 0.02 mol) in ether (25 ml). A solid separated, and the mixture was stirred and refluxed in an atmosphere of nitrogen for 7 hr. The complex was decomposed (ice-cold ammonium chloride solution), the mixture just acidified and extracted with ether. The aqueous layer was made strongly alkaline, ammonium chloride added, and the mixture extracted with ether. This ethereal extract was dried (anhydrous sodium sulphate) and on distillation gave two fractions: (1) b.p. 87–89 °C/0.04 mm, colourless mobile oil, n_D^{15} 1.5503 (0.95 g, 20% yield), unchanged Mannich base (dihydrochloride: m.p. and mixed m.p.). (2) b.p. 150–155 °C/0.04 mm, yellow viscous oil, n_D^{16} 1.5986 (1.75 g, 41% yield calc. on recovered Mannich base).

A solution of the oil in chloroform was neutralized at 0 °C with alcoholic hydrogen chloride, and the salt precipitated by addition of ether. Recrystallization from ethanol at 55–65 °C gave colourless cubes of the *propanol dihydrochloride*, m.p. 194 °C (decomp.) (Found: N, 7.3; Cl, 17.8%. Calc. for $C_{14}H_{20}ON_2S_2 \cdot 2HCl$: N, 7.2; Cl, 18.0%). The *di-acid oxalate*, from alcoholic solutions of the base and anhydrous oxalic acid, crystallized as plates, m.p. 224 °C (decomp.) (Found: N, 5.9%. Calc. for $C_{14}H_{20}ON_2S_2 \cdot 2C_2H_2O_4$: N, 5.7%).

(d) *1,1-Di- α -thienyl-3-(4'-methyl-1'-piperazino)prop-1-ene*.—Excess of dry hydrogen chloride was passed into a cold solution of the preceding propanol in chloroform. Addition of dry ether gave the *propene dihydrochloride* as colourless plates, m.p. 132 °C, which readily decolorized a solution of bromine in carbon tetrachloride (Found: N, 7.3; Cl, 18.6%. Calc. for $C_{14}H_{20}N_2S_2 \cdot 2HCl$: N, 7.4; Cl, 18.8%). Recrystallization from ethanol-ether afforded a second form of the *propene dihydrochloride* crystallizing as needles, m.p. 191 °C (Found: N, 7.1; Cl, 18.4%). This sample also readily decolorized a solution of bromine in carbon tetrachloride. The same substance (m.p. 191 °C) was obtained by boiling an alcoholic solution of the propanol dihydrochloride (m.p. 194 °C); a mixed m.p. with the propanol dihydrochloride gave m.p. 175–178 °C. The *propene di-acid oxalate* formed plates from ethanol, m.p. 213–214 °C (decomp.) (Found: N, 5.6%. Calc. for $C_{14}H_{20}N_2S_2 \cdot 2C_2H_2O_4$: N, 5.7%).

(e) *3-(4'-Methyl-1'-piperazino)-1-phenylpropan-1-one*.—Prepared in the manner described in Section II (a), from 1-methylpiperazine dihydrochloride (8.5 g; 0.05 mol), paraformaldehyde (2.1 g; 0.07 mol), and acetophenone (7.2 g; 0.05 mol) in absolute ethanol, the *Mannich base dihydrochloride* (9.5 g, 63% yield) crystallized in needles, m.p. 197 °C (Found: N, 8.9%. Calc. for $C_{14}H_{20}N_2O \cdot 2HCl$: N, 9.2%). The *base* obtained from this salt had b.p. 50–56 °C/0.05 mm, n_D^{19} 1.5451. On standing it solidified to crystals, m.p. 40–41 °C (Found: N, 11.7%. Calc. for $C_{14}H_{20}N_2O$: N, 12.0%). The *dipicrate* crystallized from 2-ethoxyethanol in needles, m.p. 264 °C (Found: N, 16.2%. Calc. for $C_{14}H_{20}N_2O \cdot 2C_6H_3N_5O_7$: N, 16.2%).

(f) *1,1-Diphenyl-3-(4'-methyl-1'-piperazino)propan-1-ol*.—To an ice-cold solution of phenylmagnesium bromide, from bromobenzene (24 g; 0.153 mol) and magnesium (3.5 g; 0.146 mol) in ether (100 ml), the above finely powdered Mannich base dihydrochloride (11 g; 0.036 mol) was added in small portions at a time. A vigorous reaction ensued with the formation of a white precipitate, and the mixture was stirred, and refluxed for 3 days. Decomposition by addition of ice-cold ammonium chloride solution, concentrated (0.880) ammonia solution, and ether extraction gave, on distillation of the dried ethereal extracts, three fractions: (1) b.p. 50–58 °C/0.01 mm, unchanged Mannich base (1.67 g, 24% yield); (2) b.p. 120–140 °C/0.01 mm, pale yellow viscous oil (0.18 g, 2% yield), n_D^{19} 1.5837, which solidified on standing to give needles, m.p. 63 °C, of *1,1-diphenyl-3-(4'-methyl-1'-piperazino)prop-1-ene* (Found: N, 9.5%. Calc. for $C_{20}H_{22}N_2$: N, 9.6%); (3) b.p. 148–154 °C/0.01 mm, solidifying to pale yellow plates (3.5 g, 52% yield calculated on recovered Mannich base). Crystallization from light petroleum (b.p. 60–90 °C) gave crystals, m.p. 117–119 °C, of *1,1-diphenyl-3-(4'-methyl-1'-piperazino)propan-1-ol* (Found: N, 8.8%. Calc. for $C_{20}H_{24}N_2O$: N, 9.0%). Cautious neutralization of a solution of this base in cold ethanol with alcoholic hydrogen chloride, followed by addition of ether, afforded the *propanol dihydrochloride*, m.p. 221 °C (Found: N, 7.3%. Calc. for $C_{20}H_{24}N_2O \cdot 2HCl$: N, 7.3%). Attempted recrystallization caused dehydration. The *propanol di-acid oxalate* had m.p. 210 °C (Found: N, 5.6%. Calc. for $C_{20}H_{24}N_2O \cdot 2C_2H_2O_4$: N, 5.7%). The *dipicrate*

had m.p. 236 °C (Found: N, 14.5%. Calc. for $C_{20}H_{24}N_2O \cdot 2C_6H_5N_3O$; N, 14.5%); again attempted recrystallization resulted in dehydration.

(g) *1,1-Diphenyl-3-(4'-methyl-1'-piperazino)prop-1-ene*.—The reaction mixture obtained from bromobenzene (15.3 g; 0.096 mol), magnesium (1.9 g; 0.08 mol), and the Mannich base (V; R=Ph) dihydrochloride (7.4 g; 0.024 mol) in the manner described above was decomposed by addition of ammonium chloride solution and then strongly acidified with concentrated hydrochloric acid. Non-basic material was removed by ether extraction and the aqueous layer strongly basified with 40% sodium hydroxide solution. Ammonium chloride was added and the mixture extracted with ether. Distillation gave two fractions: (1) b.p. 46–56 °C/0.045 mm, unchanged Mannich base (1.65 g, 30% yield); (2) b.p. 148–154 °C/0.045 mm, yellow viscous oil (3.05 g, 59% yield calculated on recovered Mannich base), which on standing solidified to the *propene*, m.p. 63 °C. Its *dihydrochloride* crystallized from ethanol in cubes, m.p. 232 °C (decomp.) (Found: N, 7.4; Cl, 19.0%. Calc. for $C_{20}H_{24}N_2 \cdot 2HCl$: N, 7.6; Cl, 19.4%) and the *dipicrate* as needles from 2-ethoxyethanol, m.p. 241 °C (decomp.) (Found: N, 14.7%. Calc. for $C_{20}H_{24}N_2 \cdot 2C_6H_5N_3O$; N, 14.9%).

(h) *3-(4'-Methyl-1'-piperazino)-1-phenyl-1- α -thienylprop-1-ol*.—The Mannich base (V; R= α -thienyl) dihydrochloride (14 g; 0.045 mol) was condensed with phenylmagnesium bromide (from 3.5 g of magnesium) exactly as in Section II (f), except the mixture was refluxed for 48 hr. Distillation of the ethereal extracts gave three fractions: (1) b.p. 50–54 °C/0.005 mm, (1.8 g, 17% yield), unchanged Mannich base; (2) b.p. 124–126 °C/0.005 mm, $n_D^{17.5}$ 1.5865 (3.0 g, 27% yield calc. on recovered Mannich base) of the *propene* (see below), which readily decolorized bromine; (3) b.p. 172–180 °C/0.005 mm, $n_D^{17.5}$ 1.605 (3.0 g, 25% yield) which solidified on standing and crystallized from light petroleum (b.p. 40–70 °C) in needles, m.p. 74–75 °C, of the *propanol* (Found: N, 8.4%. Calc. for $C_{18}H_{22}N_2OS$: N, 8.8%). This did not decolorize bromine. Neutralization of an alcoholic solution of this base with alcoholic hydrogen chloride gave the *propanol dihydrochloride*, m.p. 195–197 °C (Found: N, 7.2; Cl, 18.0%. Calc. for $C_{18}H_{22}N_2OS \cdot 2HCl$: N, 7.2; Cl, 18.2%). Attempted recrystallization resulted in dehydration, giving a *dihydrochloride*, m.p. 208–211 °C (see below), and the *propanol-diacid* had m.p. 202 °C (Found: N, 5.5; S, 6.5%. Calc. for $C_{18}H_{22}N_2OS \cdot 2C_6H_5O_4$: N, 5.6; S, 6.4%).

(i) *3-(4'-Methyl-1'-piperazino)-1-phenyl-1- α -thienylprop-1-ene*.—Fraction 2 from the above distillation partially solidified on standing and gave a *dihydrochloride* (m.p. 208–211 °C) and a *di-acid oxalate* (m.p. 196 °C) which appeared to be a mixture of isomers. The base was fractionally crystallized from light petroleum (b.p. 40–70 °C), giving a low-melting solid A and an oil B which failed to solidify.

(i) *Isomer A*. This gave a *dihydrochloride* crystallizing as needles, m.p. 216 °C (Found: N, 7.9%. Calc. for $C_{18}H_{22}N_2S \cdot 2HCl$: N, 7.6%) and a *di-acid oxalate*, m.p. 208 °C (Found: N, 5.7%. Calc. for $C_{18}H_{22}N_2S \cdot 2C_6H_5O_4$: N, 5.8%).

(ii) *Isomer B*. This base has b.p. 170 °C/0.05 mm and failed to solidify on standing (Found: N, 9.0%. Calc. for $C_{18}H_{22}N_2S$: N, 9.3%). Its *dihydrochloride* formed needles, m.p. 220 °C (Found: N, 7.5%) and a mixed m.p. with *dihydrochloride A* (m.p. 216 °C) gave m.p. 208–211 °C. The *di-acid oxalate* of B had m.p. 201 °C (Found: N, 5.6; S, 6.3%. Calc. for $C_{18}H_{22}N_2S \cdot 2C_6H_5O_4$: N, 5.8; S, 6.7%) and a mixed m.p. with *diacid oxalate A* (m.p. 208 °C) gave m.p. 196 °C.

III. ACKNOWLEDGMENTS

The authors are indebted to Professor R. H. Thorp and Mr. R. Ladd for the pharmacological results summarized in Table 2.

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SYNTHETIC ANTISPASMODICS

II. SOME ACYCLIC ANALOGUES OF PAPAVERINE

By J. CYMERMAN-CRAIG,* K. V. MARTIN,* and P. C. WAILES*

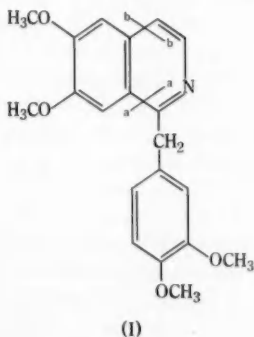
[Manuscript received February 17, 1955]

Summary

The preparation is described of four series of open-chain analogues of papaverine: *N*-alkyl- α -aminodeoxyanisoin, *N*-alkyl-2-amino-1,2-di-(*p*-methoxyphenyl)ethanols, *N*-alkyl-1,2-di-(*p*-methoxyphenyl)ethylamines, and *N*-alkyl-di-(*p*-methoxyphenyl)methylamines. All of these showed spasmolytic activity and considerably lower toxicity than papaverine.

I. INTRODUCTION

The numerous synthetic analogues of papaverine (I) which have been prepared (cf. Blicke 1944) can be divided into two main groups: (i) those with an intact *isoquinoline* ring system, e.g. "eupaverine" (Kreitmaier 1932) and "perparine" (Issekutz, Leinzinger, and Dirner 1932), and (ii) those in which the *isoquinoline* ring has been opened at the line a—a to give bis(2-phenylethyl)amines, extensively investigated by Buth, Kulz, and Rosenmund (1939) and Kulz and Rosenmund (1939), for example, "sestron" (Kulz and Rosenmund 1938).

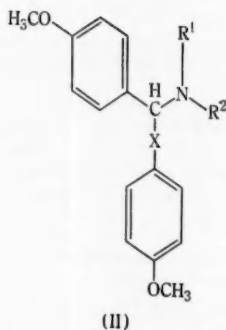


A third type of papaverine analogue, obtained by opening the *isoquinoline* ring along the line b—b, does not seem to have been investigated (except that α -diethylamino-4-methoxydeoxybenzoin and 2-amino-1,2-di-(*p*-methoxyphenyl)ethanol are reported (Mercier, Lespagnol, and Mercier 1949) to have 0.5 and 0.1

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respectively of the antispasmodic activity of papaverine in an isolated observation), and the synthesis of a group of substances of that type is now described.

A series of *N*-alkyl- α -aminodeoxyanisoin (II; X=CO), *N*-alkyl-2-amino-1,2-di-(*p*-methoxyphenyl)ethanols (II; X=CHOH), and *N*-alkyl-1,2-di-(*p*-methoxyphenyl)ethylamines (II; X=CH₂) were prepared to test whether these open-chain analogues of papaverine retain the antispasmodic activity of the parent substance.



Henne and Bruylants' (1948) method of preparation of α -bromodeoxyanisoin (in unstated yield) by the action of phosphorus tribromide on anisoin, afforded in our hands only low yields of an impure product, accompanied by much anisil, but treatment of deoxyanisoin with bromine readily gave the pure material. The *N*-alkyl- and *NN*-dialkyl- α -aminodeoxyanisoin (II; X=CO), prepared from this bromo-compound and the appropriate amine, were yellow oils decomposing in air to give anisil, but their hydrohalide salts were stable. The facile hydrolysis of the analogous α -alkylaminodeoxybenzoins and their ready oxidation to benzil was noted by Lutz, Freek, and Murphey (1948).

Reduction of the carbonyl group with aluminium isopropoxide gave the desired *N*-alkyl-2-amino-1,2-di-(*p*-methoxyphenyl)ethanols (II; X=CHOH) as stable crystalline solids, only one diastereoisomer being produced in every case.

Clemmensen reduction of α -diethylaminodeoxyanisoin resulted in hydrolytic breakdown giving 1,2-di-(*p*-methoxyphenyl)ethane and diethylamine; similar reductive fission is reported (Braun and Weissbach 1929) on Clemmensen reduction of ω -dimethylaminoacetophenone. Attempted amination of 1-chloro-1,2-di-(*p*-methoxyphenyl)ethane, prepared by a modification of Levene and Mikeska's (1925) method, proved abortive, giving 4,4'-dimethoxystilbene as sole product. This parallels the ease of dehydrohalogenation of 1-chloro-1,2-diphenylethane, which decomposes to stilbene above 50 °C (Levene and Mikeska 1925).

Goodson, Wiegand, and Splitter (1946) obtained *N*-methyl- and *N*-ethyl-1,2-di-(*p*-methoxyphenyl)ethylamine in 15 and 12 per cent. yield respectively

by the Leuckart reaction between methyl- and ethylformamide and deoxyanisoïn. The preparation of the *N*-ethyl base has now been improved (80% yield) by using lithium aluminium hydride reduction of *N*-acetyl-1,2-di-(*p*-methoxyphenyl)ethylamine (Dankova *et al.* 1951). The *N*-isopropyl base of the series (II; $X=CH_3$) was obtained in 20 per cent. yield using a modification of the method of Goodson, Wiegand, and Splitter (1946). In view of the promising activity of certain 1-phenylisoquinoline compounds, in which the methylene bridge was omitted, e.g. "neupaverine" (Kreitmaier 1932), a number of *N*-alkyl-di-(*p*-methoxyphenyl)methylamines (II; $X=$ —) were also synthesized. Diphenyl methyl bromide has been condensed (Sommelet 1922) with dimethylamine to give *NN*-dimethyldiphenylmethylamine, the diphenyl methyl bromide being prepared (Norris, Thomas, and Brown 1910) by direct bromination of diphenylmethane.

Direct bromination of di-(*p*-methoxyphenyl)methane, however, gave a dibromo-compound which analysed for $C_{15}H_{14}O_2Br_2$ and was thus di-(3-bromo-4-methoxyphenyl)methane. It proved identical with the material synthesized by condensation of 2-bromoanisole and formaldehyde, using an adaptation of the method of Robinson (1916). Although the action of phosphorus tribromide with diphenylmethanol gives diphenyl methyl bromide (Claisen 1925), application of this reaction to 4,4'-di(methoxyphenyl)methanol afforded only 4,4'-dimethoxybenzophenone. The desired 4,4'-di(methoxyphenyl)methyl bromide was however obtained by the action of dry hydrogen bromide on the alcohol, and its structure proved by reaction with isopropylamine to give *N*-isopropyl-di-(*p*-methoxyphenyl)methylamine. In view of the instability of this bromo-compound, 4,4'-di(methoxyphenyl)methyl chloride (Straus and Dutzmann 1921) was condensed with the appropriate amines, and the *N*-alkyl-di-(*p*-methoxyphenyl)methylamines isolated as stable solids. The compounds were tested by Professor R. H. Thorp, Mr. R. Ladd, and Mr. G. Thorburn of the Pharmacology Department of this University, on isolated guinea-pig ileum against spasms produced by barium chloride and carbachol, using papaverine and atropine as standards, and the relative potencies (on a molar basis) are summarized in Table 1. All compounds exhibited spasmolytic musculotropic activity, in many cases exceeding that of papaverine. Relative neurotropic activity was between 0.005 and 0.2 of atropine, and acute toxicities (intravenous in mice) were uniformly between 60 and 80 mg/kg for all series, that is, with an LD_{50} of 2 to 3 times that of papaverine (LD_{50} 30 mg/kg). In view of these promising results, further work is proceeding.

II. EXPERIMENTAL

Analyses are by (the late) Mrs. E. Bielski, University of Sydney, and Dr. K. W. Zimmermann, C.S.I.R.O. Microanalytical Laboratory.

(a) *α -Bromodeoxyanisoïn.*—A solution of deoxyanisoïn (11.45 g) in chloroform (50 ml) and ether (30 ml) was heated gradually with bromine (2.5 ml) with shaking. The solution was heated on the water-bath for 0.5 hr, cooled, washed (sodium bicarbonate and water), dried (calcium chloride), and evaporated, affording *α -bromodeoxyanisoïn* (11.5 g, 75% yield) as cream needles, m.p. 103 °C, from benzene-light petroleum (b.p. 60–80 °C) (Found: C, 57.7; H, 4.7%. Calc. for $C_{16}H_{15}O_2Br$: C, 57.3; H, 4.5%). Henne and Bruylants (1948) give m.p. 103–104 °C.

(b) α -Dimethylaminodeoxyanisoin.—A solution of α -bromodeoxyanisoin (8 g) in dry benzene (75 ml) was saturated with dry dimethylamine. The solution became warm and deposited a white solid. The mixture was kept overnight, filtered, the solid washed (benzene), and the combined filtrates extracted with hydrochloric acid (2N). The acid solution was made strongly alkaline, extracted with ether, and the ethereal extracts washed (water), dried (sodium sulphate), and evaporated, leaving a light yellow viscous oil (6.4 g, 90% yield) which tended to decompose on standing in air. The *hydriodide*, prepared by treatment of the hydrochloride with saturated potassium iodide solution, crystallized from ethanol-ethyl acetate as prisms, m.p. 169 °C (Found: C, 51.0; H, 5.5; N, 3.5%. Calc. for $C_{18}H_{21}O_3N.HI$: C, 50.6; H, 5.2; N, 3.3%).

(c) α -Methylaminodeoxyanisoin.—The base (90% yield) had b.p. 190 °C/0.001 mm, n_D^{17} 1.6040. The *hydrochloride* crystallized from ethanol as rosettes of needles, m.p. 235–236 °C (Found: Cl, 10.9%. Calc. for $C_{17}H_{19}O_3N.HCl$: Cl, 11.0%).

(d) α -Diethylaminodeoxyanisoin.—The base (94% yield) had b.p. 168–173 °C/0.06 mm (Found: C, 72.9; H, 7.9; N, 4.3%. Calc. for $C_{20}H_{25}O_3N$: C, 73.3; H, 7.7; N, 4.3%). After standing in air for several days, a yellow solid was formed, m.p. 131 °C, undepressed on admixture with anisil.

The *hydriodide*, obtained from the hydrochloride with sodium iodide in acetone, crystallized from water as prisms, m.p. 140 °C (Found: C, 52.5; H, 5.9; N, 3.0%. Calc. for $C_{20}H_{25}O_3N.HI$: C, 52.7; H, 5.8; N, 3.1%).

(e) α -Ethylaminodeoxyanisoin.—The base (85% yield) had b.p. 183 °C/0.001 mm, $n_D^{16.5}$ 1.5922, and the *hydriodide* crystallized from ethanol-ethyl acetate as prisms, m.p. 187–188 °C (Found: C, 50.6; H, 5.2%. Calc. for $C_{18}H_{21}O_3N.HI$: C, 50.9; H, 5.3%).

(f) α -isoPropylaminodeoxyanisoin.—This base (90% yield) had b.p. 182 °C/0.001 mm, $n_D^{20.5}$ 1.5818 and the *hydriodide* separated from water as prisms, m.p. 100 °C (Found: C, 49.2; H, 5.8%. Calc. for $C_{19}H_{23}O_3N.HI.1.5H_2O$: C, 48.8; H, 5.6%).

(g) 2-Methylamino-1,2-di-(p-methoxyphenyl)ethanol.—A mixture of α -methylaminodeoxyanisoin (3.6 g), aluminium isopropoxide (10 g), and isopropanol (25 ml) was refluxed for 17 hr, when the distillate was free from acetone. Most of the solvent was removed, the residue decomposed with sulphuric acid (2N), the solution basified and extracted with ether. Distillation gave the base (3.2 g, 90% yield) as a colourless oil, b.p. 180 °C/0.001 mm, which solidified and crystallized from benzene-light petroleum as needles, m.p. 127–128 °C (Found: C, 71.5; H, 7.0; N, 5.1%. Calc. for $C_{17}H_{21}O_3N$: C, 71.1; H, 7.3; N, 4.9%).

(h) 2-Ethylamino-1,2-di-(p-methoxyphenyl)ethanol.—The base was an oil (95% yield), b.p. 180 °C/0.001 mm, which solidified to needles (from light petroleum), m.p. 114 °C (Found: C, 71.7; H, 7.4%. Calc. for $C_{18}H_{23}O_3N$: C, 71.7; H, 7.7%).

(i) 2-isoPropylamino-1,2-di-(p-methoxyphenyl)ethanol.—The base (90% yield) had b.p. 170–174 °C/0.001 mm and solidified, crystallizing from light petroleum (b.p. 60–90 °C) as needles, m.p. 124 °C (Found: C, 72.8; H, 7.6; N, 4.5%. Calc. for $C_{19}H_{23}O_3N$: C, 72.4; H, 8.0; N, 4.5%).

(j) 2-Diethylamino-1,2-di-(p-methoxyphenyl)ethanol.—The base (98% yield) had n_D^{15} 1.5613, solidifying, and crystallizing from light petroleum (b.p. 40–70 °C) as rectangular prisms, m.p. 75 °C (Found: C, 72.8; H, 8.2; N, 4.3%. Calc. for $C_{20}H_{27}O_3N$: C, 72.9; H, 8.2; N, 4.2%). The *hydriodide* crystallized from water as needles, m.p. 189 °C (Found: C, 52.6; H, 6.3; N, 3.5%. Calc. for $C_{20}H_{27}O_3N.HI$: C, 52.5; H, 6.2; N, 3.1%).

(k) 2-Dimethylamino-1,2-di-(p-methoxyphenyl)ethanol.—The *hydrochloride* crystallized from ethanol as needles, m.p. 248 °C (decomp.) (Found: C, 64.1, 64.2; H, 7.5, 7.6; N, 4.0; Cl, 11.0%. Calc. for $C_{18}H_{23}O_3N.HCl$: C, 64.0; H, 7.2; N, 4.1; Cl, 10.5%) and the *hydriodide* formed needles, m.p. 211 °C, from ethanol-ethyl acetate (Found: C, 50.6; H, 5.8; N, 3.5%. Calc. for $C_{18}H_{23}O_3N.HI$: C, 50.4; H, 5.6; N, 3.3%).

(l) Clemmensen Reduction of α -Diethylaminodeoxyanisoin.—A mixture of α -diethylaminodeoxyanisoin (3.1 g), hydrochloric acid (12 ml; 5N), and amalgamated zinc (6 g) was refluxed

for 7.5 hr, adding hydrochloric acid (0.7 ml; 10N) every hr. The mixture was filtered and the filtrate made strongly alkaline and extracted with ether. The ethereal extracts left no residue. The aqueous washings, neutralized with benzenesulphonic acid, gave diethylammonium benzenesulphonate, m.p. and mixed m.p. 139 °C.

The undissolved portion was extracted with benzene, giving 1,2-di-(*p*-methoxyphenyl)ethane (2.9 g, 100% yield), crystallizing from methanol as prisms, m.p. and mixed m.p. 123 °C.

(m) *Reaction of Diethylamine with 1-Chloro-1,2-di-(p-methoxyphenyl)ethane*.—1,2-Di-(*p*-methoxyphenyl)ethanol (1 g) (Buck and Jenkins 1929) was added gradually to ice-cold thionyl chloride (1.5 ml) and the solution was kept for 3 hr. Thionyl chloride was removed *in vacuo* below 40 °C and the residue triturated with ether. The resulting solid was filtered off, dissolved in dry benzene (15 ml), and treated with diethylamine (0.3 g). A white precipitate appearing almost immediately was 4,4'-dimethoxystilbene, m.p. and mixed m.p. 210 °C. The filtrate contained no base other than diethylamine.

(n) *1,2-Di-(p-methoxyphenyl)ethylamine*.—The base had m.p. 101–102 °C (Dankova *et al.* 1951 give m.p. 98 °C) and the hydrochloride crystallized from ethanol as needles, m.p. 212 °C (Found: C, 65.4; H, 6.9%. Calc. for $C_{18}H_{20}O_2N.HCl$: C, 65.4; H, 6.9%). Dankova *et al.* (1951) give m.p. 203–204 °C.

(o) *N-Ethyl-1,2-di-(p-methoxyphenyl)ethylamine*.—(i) Acetylation of 1,2-di-(*p*-methoxyphenyl)ethylamine gave the acetyl derivative, needles from aqueous ethanol, m.p. 158 °C (Found: C, 72.3; H, 7.0%. Calc. for $C_{18}H_{21}O_2N$: C, 72.7; H, 7.1%). Dankova *et al.* (1951) give m.p. 151–152 °C.

(ii) The acetyl compound (5 g; 0.016 mol), placed in the thimble of a Soxhlet apparatus, was gradually extracted into a boiling ethereal solution of lithium aluminium hydride (4.5 g; 0.012 mol). After 7 hr, excess reagent was decomposed, the solution filtered, and removal of solvent from the dried filtrate gave the base (3.7 g, 80% yield), m.p. 60 °C. The hydrochloride had m.p. 167 °C. Goodson, Wiegand, and Splitter (1946) give 12% yield, m.p. 167–169 °C.

(p) *N-isopropyl-1,2-di-(p-methoxyphenyl)ethylamine*.—To formic acid (8 g; 4 mol; 100%) was added with cooling isopropylamine (9.4 g; 4 mol) followed by deoxyanisoin (10 g; 1 mol) and acetic acid (1 ml). Water was distilled off, and heating continued for a further 3 hr during which the temperature rose slowly to 205 °C. After refluxing with hydrochloric acid (50 ml; 2N) for 1 hr, the mixture was extracted with boiling water (2 × 50 ml), and the combined aqueous extracts basified and extracted with ether. Removal of solvent gave the base (1.8 g, 20% yield), m.p. 47–48 °C converted to the *hydriodide*, crystallizing from ethanol-ethyl acetate as plates, m.p. 177–178 °C (Found: C, 53.6; H, 6.2%. Calc. for $C_{18}H_{21}O_2N.HI$: C, 53.4; H, 6.1%).

(q) *Bromination of Di-(p-methoxyphenyl)methane*.—A solution of di-(*p*-methoxyphenyl)methane (2.28 g; 0.01 mol) in chloroform (16 ml) was treated dropwise with bromine (0.7 ml; 0.014 mol). The solution warmed and hydrogen bromide was evolved. After refluxing for 0.5 hr, the cooled mixture was washed (sodium bicarbonate), dried (calcium chloride), and the solvent removed, giving needles (2.7 g, 100% yield calc. on bromine used) from light petroleum (b.p. 60–90 °C), m.p. 101.5 °C (Found: C, 46.6; H, 4.1%. Calc. for $C_{15}H_{14}O_2Br_2$: C, 46.7; H, 3.8%) of di-(3-bromo-4-methoxyphenyl)methane.

(r) *Synthesis of Di-(3-bromo-4-methoxyphenyl)methane*.—An aqueous formaldehyde solution (15 ml; 40%) was added to an ice-cold mixture of 2-bromoanisole (10 g) and sulphuric acid (90 g; 80% w/v), the mixture shaken for 3 hr, and the precipitated solid crystallized from light petroleum, giving needles, m.p. 101 °C undepressed on admixture with the product obtained in Section II (q).

(s) *Attempted Bromination of 4,4'-Di-(methoxyphenyl)methanol*.—(i) A stirred and cooled mixture of 4,4'-di-(methoxyphenyl)methanol (8.1 g; 2 mol), benzene (25 ml) and pyridine (5 ml) was gradually treated at 0 °C with phosphorus tribromide (4.5 g; 1 mol) in benzene (5 ml). A yellow solid settled out. After a further 3 hr stirring, the mixture was extracted with chloroform and distillation of the washed (sodium bicarbonate and water) and dried (calcium chloride) extracts gave a product (3 g), b.p. 169–171 °C/0.5 mm, crystallizing from light petroleum

(b.p. 60–90 °C) as needles, m.p. 141 °C undepressed on admixture with 4,4'-dimethoxybenzophenone.

(ii) Treatment of 4,4'-di(methoxyphenyl)methanol in carbon tetrachloride with phosphorus tribromide, followed by working-up as before, gave 4,4'-dimethoxybenzophenone (m.p. and mixed m.p.).

(t) 4,4-Di-(methoxyphenyl)methyl Bromide.—4,4'-Di(methoxyphenyl)methanol (7 g) in benzene (60 ml) over calcium chloride (5 g) was saturated with dry hydrogen bromide, and allowed to stand 4 hr. Evaporation in a vacuum desiccator and extraction of the residual

TABLE I
SPASMOLYTIC ACTIVITIES

Compound II			Relative Potency (M)
X	R ¹	R ²	
CO	H	Me	0.9
CO	H	Et	1.2
CO	H	isoPr	0.3
CO	Me	Me	3.3*
CO	Et	Et	0.2*
CHOH	H	Me	0.8
CHOH	H	Et	0.8
CHOH	H	isoPr	0.5
CHOH	Me	Me	0.2*
CHOH	Et	Et	1.2*
CH ₂	H	H	0.8
CH ₂	H	Et	0.9
CH ₂	H	isoPr	1.2
—	H	H	0.8
—	H	Me	1.8
—	H	Et	0.8
—	H	isoPr	0.6
—	Me	Me	1.1
—	Et	Et	1.0
Papaverine	—	—	1.0

* Spasm of the guinea-pig ileum was induced with posterior pituitary extract.

red oil with light petroleum (b.p. 60–90 °C) afforded 4,4'-di(methoxyphenyl)methyl bromide (4 g, 46% yield) as colourless prisms, m.p. 70 °C, rapidly turning pink (Found: C, 58.8; H, 4.9%. Calc. for C₁₅H₁₃O₂Br: C, 58.7; H, 4.9%). Treatment of this bromo-compound (1 g) in dry benzene (10 ml) with isopropylamine (1.5 ml) and working-up as described in Section II (b) afforded *N*-isopropyl-di-(*p*-methoxyphenyl)methylamine (0.6 g, 64% yield), m.p. and mixed m.p. 63 °C (see below).

(u) *N*-Methyl-di-(*p*-methoxyphenyl)methylamine.—A solution of 4,4'-di(methoxyphenyl)methyl chloride in benzene was saturated with methylamine. Working-up as in Section II (b) gave the base (90% yield) as needles, m.p. 49–50 °C, from aqueous ethanol (Found: C, 74.7; H, 7.4%. Calc. for C₁₆H₁₉O₂N: C, 74.9; H, 7.5%). The *toluene-p*-sulphonyl derivative crystallized from

ethanol as needles, m.p. 115 °C (Found : C, 67.0; H, 6.2%. Calc. for $C_{23}H_{25}O_4NS$: C, 67.1; H, 6.1%).

(v) *N-Ethyl-di-(p-methoxyphenyl)methylamine*.—The base had b.p. 149 °C/0.01 mm, m.p. 38.5 °C (Found : C, 75.2; H, 7.6%. Calc. for $C_{17}H_{21}O_2N$: C, 75.2; H, 7.8%). The benzoyl derivative (needles from ethanol) had m.p. 140 °C (Found : C, 76.6; H, 6.7%. Calc. for $C_{24}H_{25}O_3N$: C, 76.8; H, 6.7%).

(w) *NN-Dimethyl-di-(p-methoxyphenyl)methylamine*.—The base (needles from aqueous ethanol) had m.p. 86.5 °C (Found : C, 75.7; H, 7.7%. Calc. for $C_{17}H_{21}O_2N$: C, 75.2; H, 7.8%) and the hydriodide formed needles from ethyl acetate, m.p. 186 °C (decomp.) (Found : C, 51.2; H, 5.6%. Calc. for $C_{17}H_{21}O_2N.HI$: C, 51.6; H, 6.0%).

(x) *NN-Diethyl-di-(p-methoxyphenyl)methylamine*.—The base formed needles, m.p. 57 °C, from aqueous ethanol (Found : C, 76.2; H, 8.4; N, 4.7%. Calc. for $C_{19}H_{25}O_2N$: C, 76.3; H, 8.4; N, 4.9%). The hydrochloride (needles from water) had m.p. 105 °C (Found : C, 66.4; H, 7.9%. Calc. for $C_{19}H_{25}O_2N.HCl.H_2O$: C, 66.4; H, 7.6%).

(y) *N-isoPropyl-di-(p-methoxyphenyl)methylamine*.—The base crystallized from aqueous ethanol as needles, m.p. 63 °C (Found : C, 75.8; H, 8.1; N, 4.8%. Calc. for $C_{18}H_{23}O_2N$: C, 75.9; H, 8.0; N, 5.0%) and the hydriodide formed needles from aqueous ethanol, m.p. 100 °C (Found : C, 51.5; H, 6.2%. Calc. for $C_{18}H_{23}O_2N.HI.0.5 H_2O$: C, 51.2; H, 5.9%).

III. ACKNOWLEDGMENTS

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IODINATION OF *N*-METHYLQUINOLINIUM SALTS

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Summary

Iodination of *N*-methylquinaldinium iodide gives *N*-methylquinaldinium tri-iodide which with silver nitrate affords quinoline-2-aldehyde methiodide. A possible mechanism is advanced. Iodination of *N*-methyl-lepidinium iodide similarly yields *N*-methyl-lepidinium tri-iodide, but in this case silver nitrate treatment gives no aldehyde. Excess of iodine results in the diamagnetic bis(*N*-methyl-lepidinium)octa-iodide. The evidence obtained from absorption spectra and electrical conductivity measurements regarding ionic and intraionic dissociation of *N*-methylquinolinium polyiodides is discussed.

I. INTRODUCTION

In a series of papers, Hammick and his co-workers (Hammick 1923 ; Dyson and Hammick 1939 ; Brown, Hammick, and Thewlis 1951) have investigated the side-chain halogenation of methylquinolines. The ω -tribromination and trichlorination of quinaldine were readily accomplished by free halogen (Hammick 1923) but no ω -iodo-derivatives are yet known (Brown, Hammick, and Thewlis 1951).

Quaternization of the nitrogen atom in quinaldine enhances the reactivity of the 2-methyl group (cf. Bergstrom 1944), and *N*-methylquinaldinium iodide easily underwent iodination with 1, 2, or 3 moles of iodine, giving the same product (m.p. 142 °C) analysing correctly for *N*-methyl- ω -di-iodoquinaldinium iodide(I) in 95 per cent. yield, irrespective of whether or not the reaction was buffered with sodium acetate. The same substance (97 per cent. yield) was obtained using sodium nitrite and hydriodic acid, and (95 per cent. yield) when the methiodide was added to 6 or more moles of iodine at 70–80 °C. The failure to give the expected ω -tri-iodomethyl derivative could be attributed to the large size of the iodine atom, making it impossible for this compound to exist due to steric interference between the tri-iodomethyl and *N*-methyl group. This is also shown in the atomic model of I (Fig. 1).

In view of the well-known tendency of iodine to form the tri-iodide ion, an alternative structure to I could be *N*-methylquinaldinium tri-iodide (II), and the reactions of the substance were examined. The compound was stable to crystallization from chloroform or ethanol, or chromatography on alumina, but was slowly decomposed by boiling acetone forming iodoacetone. It was pleochroic under the polarizing microscope. Treatment with excess of silver nitrate (which gave 3 moles of silver iodide), followed by sodium chloride,

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afforded quinoline-2-aldehyde methochloride (2,4-dinitrophenylhydrazones), converted (sodium iodide in absolute ethanol) to quinoline-2-aldehyde methiodide. The phenylhydrazone methiodide obtained from the latter readily eliminated methyl iodide giving quinoline-2-aldehyde phenylhydrazone identical with an authentic specimen. Further proof was afforded by synthesis of the aldehyde phenylhydrazone methiodide. Attempted methylation of quinoline-2-aldehyde, and selenium dioxide oxidation of *N*-methylquinaldinium iodide, failed, but condensation of nitrosobenzene with *N*-methylquinaldinium iodide and hydrolysis of the resulting Schiff's base in the presence of phenylhydrazine gave the phenylhydrazone methiodide.

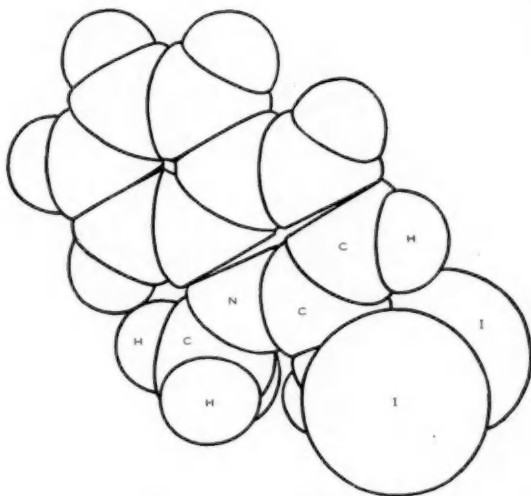


Fig. 1.—Molecular model of *N*-methyl- ω -di-iodoquinaldinium ion.

However, attempted conversion of the compound, m.p. 142 °C, into *N*-methyl- ω -dichloroquinaldinium chloride by action of silver chloride failed, and treatment with lithium picrate gave *N*-methylquinaldinium picrate, also obtained when silver picrate was employed. The infra-red spectrum of the compound, m.p. 142 °C, in the region of 533 cm^{-1} (the reported frequency of the C—I bond in methyl iodide) showed bands at 494, 520, and 572 cm^{-1} ; *N*-methylquinaldinium iodide absorbed at 504, 519, and 573 cm^{-1} ; none of these bands was intense, and the compound, m.p. 142 °C, thus was devoid of C—I bonds. Support for structure II was obtained from the ultraviolet absorption spectrum. The pale yellow solution in 95 per cent. ethanol showed maxima at 2380, 2940, and 3580 Å, identical with those of *N*-methylquinolinium tri-iodide. The tri-iodide ion is known (Gilbert, Goldstein, and Lowry 1931) to absorb at 2900 and 3580–3600 Å. The spectrum of *N*-methylquinaldinium tri-iodide in chloroform

solution, however, showed (in the 2600–4000 Å region) only a single band, at 3220 Å, identical with that of *N*-methylquinaldinium iodide (Sutherland and Compton 1952). The colour of this solution was violet, and removal of iodine from tri-iodide compounds by solvents such as carbon tetrachloride is known (Cremer and Duncan 1931).

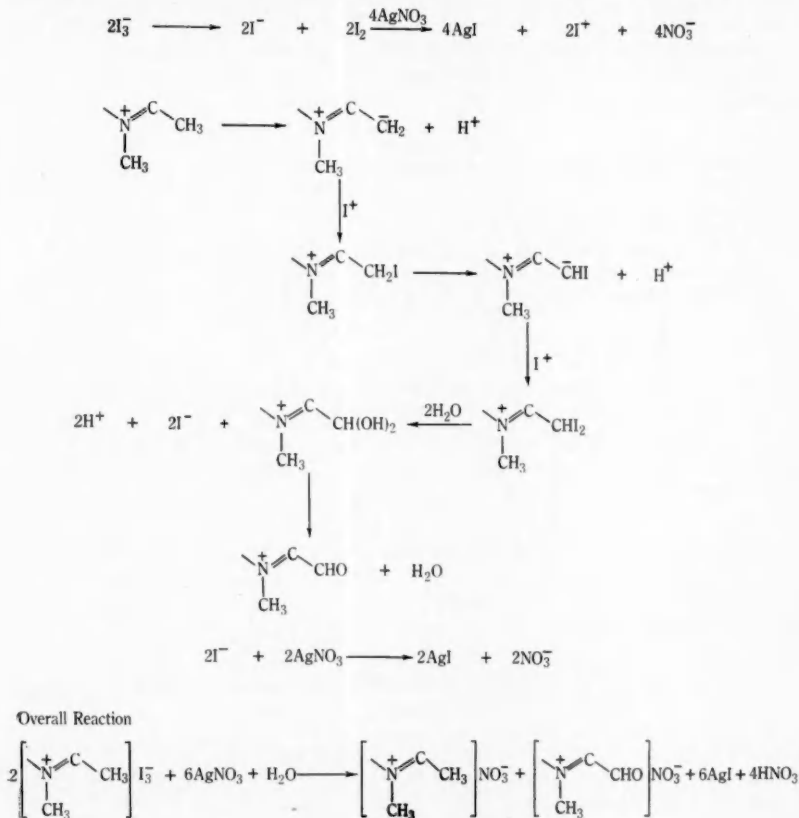
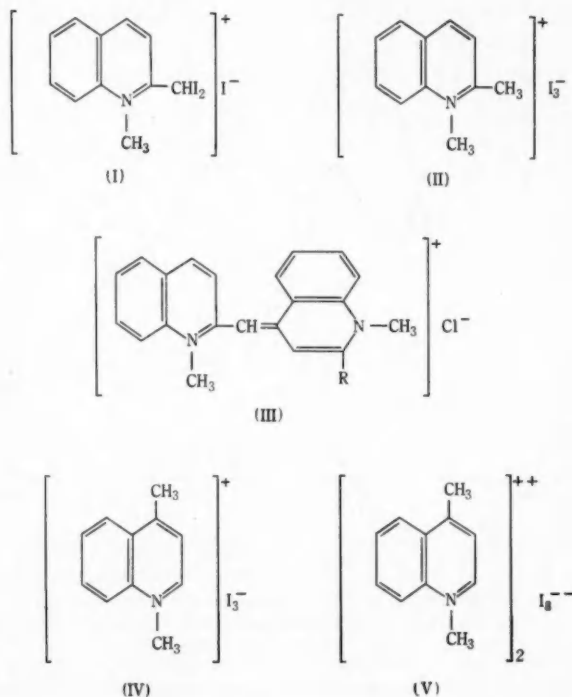


Fig. 2

The action of silver nitrate on *N*-methylquinaldinium tri-iodide to give quinoline-2-aldehyde methiodide implies fission of tri-iodide ion into iodide ion and iodine, the latter reacting with silver nitrate to give the iodonium (I^+) ion. This or its hydrated equivalent, the hypoiodous acidium ion (H_2IO^+) is known (Ingold 1953) to be the active agent in iodination. Attack of this ion on the reactive 2-methyl group in the quinaldinium ion or on its methylene base would give first the 2-iodomethyl and then (by a repetition of this process, which

would proceed at an enhanced rate due to the electron-attracting character of the halogen atom) the 2-di-iodomethyl compound; steric considerations do not permit the formation of the tri-iodomethyl compound. The di-iodomethyl compound would be expected to undergo a rapid hydrolysis, probably by an SN_1 mechanism in the manner envisaged for benzal chloride (Alexander 1950), to give the metho-salt of quinoline-2-aldehyde hydrate; quinoline-2-aldehyde itself is known to form a stable hydrate (Ramsey 1951). The reaction is outlined in Figure 2; the process clearly goes to completion due to the removal, by excess of silver nitrate, of tri-iodide ion to form insoluble silver iodide.



In agreement with the postulated mechanism are (i) the amount of silver iodide produced, (ii) the marked acidity of the mixture at the end of the reaction, and (iii) the result of the action of alkali on the final reaction mixture, which afforded a brown solid, changed in air to a brilliant blue dye, $C_{22}H_{19}O_2N_2Cl$. Under the same conditions *N*-methylquinaldinium iodide afforded a blue isocyanine dye, $C_{22}H_{21}N_2Cl$, which must be 1,1'-dimethyl-2'-methylisocyanine chloride (III; $R=CH_3$). Both dyes showed identical absorption spectra, with a single maximum at 5630 Å, closely resembling that of pinaverdol (1,6,1'-trimethylisocyanine iodide) which has λ_{max} 5620 Å (Wise and Adams 1918;

Wise *et al.* 1919), and therefore contains the same chromophore. The dye $C_{22}H_{19}O_2N_2Cl$ must thus be 1,1'-dimethylisocyanine chloride 2'-carboxylic acid (III; $R=COOH$), formation of which implies oxidation of the aldehyde pseudo-base first formed, to *N*-methyl-4-quinolone-2-carboxylic acid followed by condensation of this with the equimolecular proportion of unchanged *N*-methylquinaldinium ion postulated in the above mechanism giving the dye (III; $R=COOH$). Only in this way can formation of this dye be accounted for.

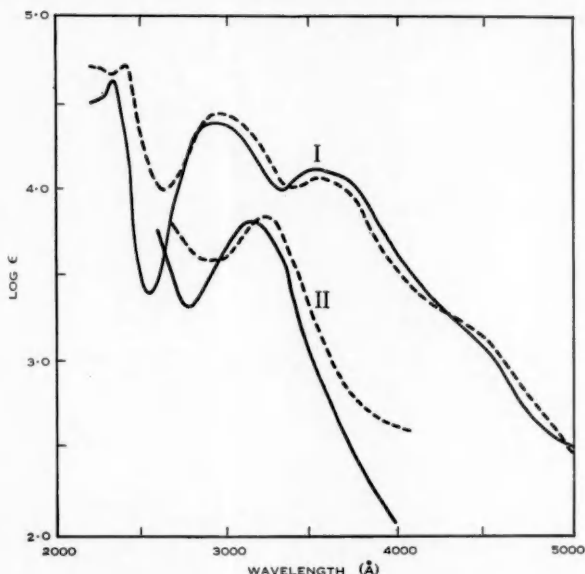


Fig. 3.—Curve I, — *N*-Methyl-lepidinium tri-iodide in ethanol.
 --- *N*-Methylquinaldinium tri-iodide in ethanol.
 Curve II, — *N*-Methyl-lepidinium tri-iodide in chloroform.
 --- *N*-Methylquinaldinium tri-iodide in chloroform.

Although reaction of quinoline-2-aldehyde methochloride with iodide ion in *absolute* ethanol gave the expected aldehyde methiodide, the same methochloride, with excess iodide ion in *aqueous* ethanol, afforded *N*-methylquinaldinium tri-iodide (II). In presence of excess of iodide ion, attack of iodide on the dihydroxymethyl group of the aldehyde hydrate must therefore result in reduction to the 2-methyl compound, free iodine being produced presumably via hypiodous acid. In this case, the driving force must be the conversion of iodine to insoluble *N*-methylquinaldinium tri-iodide.

Treatment of *N*-methyl-lepidinium iodide with 1 mole of iodine gave a quantitative yield of *N*-methyl-lepidinium tri-iodide (IV) which reacted with silver nitrate to give *N*-methyl-lepidinium nitrate, the lack of any aldehydic product being clearly due to the lower reactivity of the 4-methyl group over

that in the 2-position (Bergstrom 1944). *N*-Methyl-lepidinium nitrate was converted by lithium picrate into *N*-methyl-lepidinium picrate, also produced by the same reagent from *N*-methyl-lepidinium tri-iodide. The ultraviolet spectrum of *N*-methyl-lepidinium tri-iodide was identical with that of the corresponding quinaldinium compound; its pale yellow ethanolic solution showing the 2330 Å maximum and the two maxima (2950 and 3580 Å) characteristic of the tri-iodide ion, while the violet chloroform solution gave a single maximum (3170 Å) identical with that of *N*-methyl-lepidinium iodide (Sutherland and Compton 1952).

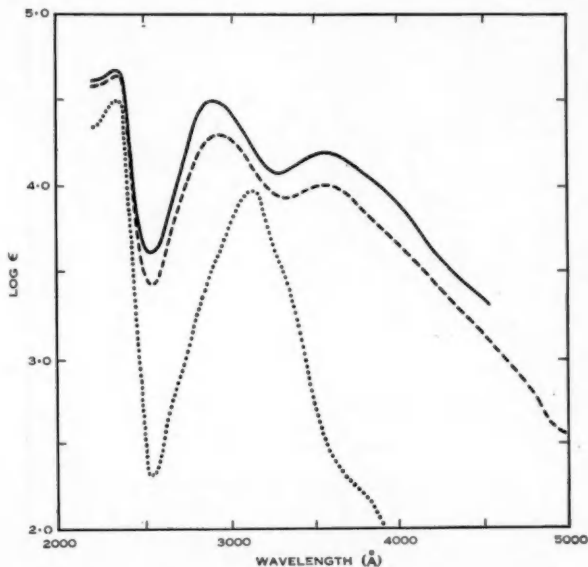


Fig. 4.— — *N*-Methylquinolinium pentaide in ethanol.
--- *N*-Methylquinolinium tri-iodide in ethanol.
.... *N*-Methylquinolinium iodide in ethanol.

When *N*-methyl-lepidinium iodide was treated with 3 moles or more of iodine, the initially-formed brown needles changed to black plates, $C_{11}H_{12}NI_4$, stable to crystallization from chloroform but decomposing in ethanol or acetone (with formation of iodoacetone), on warming to 100 °C, or on attempted chromatography on alumina, to give free iodine and *N*-methyl-lepidinium tri-iodide, which regenerated the black substance on treatment with iodine. The structure *N*-methyl-lepidinium tetraide was excluded by a measurement of the magnetic susceptibility, which showed the compound to be diamagnetic whereas a tetra-iodide ion, possessing an unpaired electron, would be paramagnetic. The compound must thus be the dimer, bis(*N*-methyl-lepidinium) octaide (V), and parallels the so-called caesium tetraide. This was shown (Hubard 1942) to be

diamagnetic, and regarded as a crystal aggregate of CsI_3 and CsI_5 , but its crystal structure has recently (Havinga, Boswijk, and Wiebenga 1954) been shown to be Cs_2I_8 , containing the flat octaiodide ion in agreement with the known facile dissociation into CsI_3 and iodine (Briggs 1930).

The ultraviolet spectrum of the octaiodide was identical with that of *N*-methyl-lepidinium tri-iodide, with an inflexion near 4500 \AA , the reported absorption maximum of iodine in ethanol (Batley 1928). A slight inflexion at 3180 \AA may be due to a further mode of dissociation giving some *N*-methyl-lepidinium iodide.

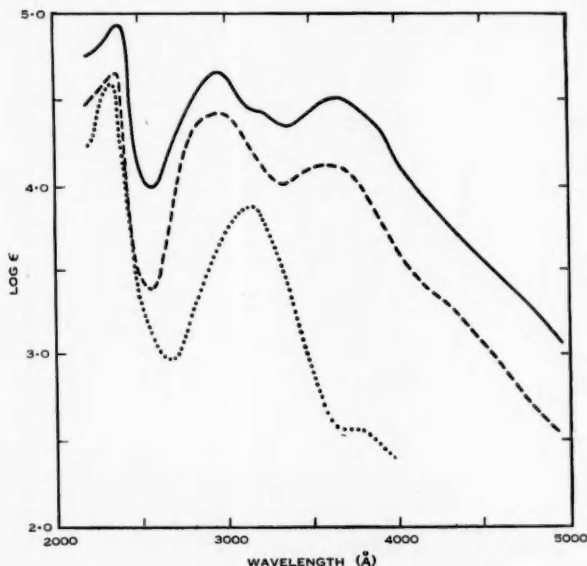


Fig. 5. — Bis(*N*-methyl-lepidinium) octaiodide in ethanol.
 --- *N*-Methyl-lepidinium tri-iodide in ethanol.
 *N*-Methyl-lepidinium iodide in ethanol.

As a model compound for molecular weight determinations, the molecular weight of *N*-methylquinolinium penta-iodide (Trowbridge 1899; Schall 1908) was examined cryoscopically in nitrobenzene, and corresponded to 16 and 29 per cent. ionic dissociation in 0.07 and 0.03M solution respectively. Schall (1908) cites a similar result, reporting a molecular weight corresponding to only 11 per cent. ionic dissociation for *N*-butylquinolinium tri-iodide in 0.09M solution in benzil. Measurements of the electrical conductivity at 20°C of solutions of *N*-methylquinolinium penta-iodide in nitrobenzene from 0.01 to 0.0001M gave parallel results, indicating that ionic dissociation was complete only at 0.0001M (Fig. 6) with a Λ_∞ value of 35.0, corresponding to complete dissociation into two ions in excellent agreement with Walden (1912) and

Creighton and Way (1918). However, conductivity measurements clearly give no indication of the nature of these ions, since dissociation, for example, of I_5^- ions into I_3^- ions and iodine would not affect the conductivity appreciably due to the low equivalent conductivity of iodine in nitrobenzene. Calculation of the results of Bruner and Galecki (1913) shows that even in moist nitrobenzene, iodine has a Λ_∞ value of only 0.9 at 18 °C.

Examination of the ultraviolet spectrum of *N*-methylquinolinium penta-iodide in ethanol (0.0001M) showed that the spectrum was, in fact, identical with that of *N*-methylquinolinium tri-iodide with the addition of a slight inflexion

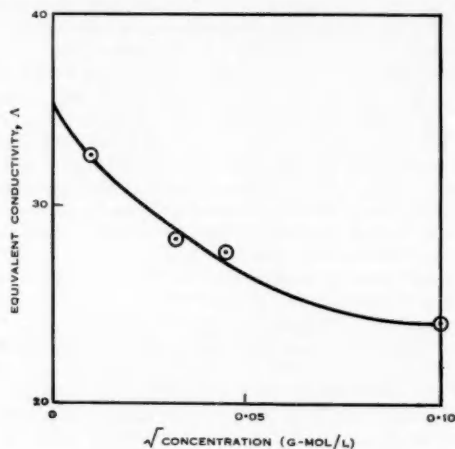


Fig. 6.—Conductivity of *N*-methylquinolinium penta-iodide in nitrobenzene at 20 °C.

near 4500 Å; the $E_{1\text{cm}}^{1\%}$ values for the two curves were identical. *N*-Methylquinolinium penta-iodide was, however, unchanged after crystallization from ethanol.

Attempted molecular weight determination of the octa-iodide (cryoscopic in nitrobenzene) gave anomalous results; this is not unexpected in view of the various possible ionic and intraionic modes of dissociation of V. The possibility that the compound is a eutectic or crystal aggregate of *N*-methyl-lepidinium tri-iodide and penta-iodide cannot be rigidly excluded; an X-ray structure determination, which may afford unequivocal proof of structure, is currently in progress in this Laboratory.

II. EXPERIMENTAL

(a) *N*-Methylquinaldinium Iodide.—The following method was found to be an improvement over that of Doebner and Miller (1883). Quinaldine (10 g), dry methanol (50 ml), and methyl iodide (12 g) were refluxed for 24 hr, more methyl iodide (5 g) being added at 8 hr intervals. Removal of solvent and addition of dry ether gave the methiodide (18.5 g, 92% yield), m.p. 195 °C. Doebner and Miller (1883) give m.p. 195 °C.

(b) *N-Methylquinaldinium Chloride*.—*N-Methylquinaldinium iodide* (2 g), silver chloride (3.5 g), and absolute ethanol (50 ml) were refluxed for 1 hr. The filtrate was concentrated *in vacuo* when dry ether precipitated the *methochloride* (1.25 g, 92% yield), crystallizing from chloroform-ether as needles, m.p. 148–149 °C (Found: N, 7.1%. Calc. for $C_{11}H_{12}NCl$: N, 7.2%).

(c) *N-Methylquinaldinium Tri-iodide*.—(i) Hydriodic acid (35 g; 55% w/w) was added dropwise to *N-methylquinaldinium iodide* (7.1 g) and sodium nitrite (5.2 g) in water (40 ml). Nitrous fumes were evolved, and the brown precipitate crystallized from methanol as red-brown plates (13.0 g, 97% yield), m.p. 141.5–142 °C (Found: C, 24.7; H, 1.9; N, 2.2; I, 70.9%. Calc. for $C_{11}H_{13}NI_3$: C, 24.5; H, 2.2; N, 2.6; I, 70.7%).

(ii) *N-Methylquinaldinium iodide* (2.85 g; 0.01 mol) and sodium acetate (10 g) in water (50 ml) were treated with iodine (5.1 g; 0.02 mol) in potassium iodide solution with vigorous stirring, continued for 0.5 hr after addition was complete. The solid was well washed (water, then dry ether) giving 5.15 g (95%) of the tri-iodide, m.p. 141.5–142 °C, undepressed with the product obtained in (i) (Found: C, 24.85; H, 2.2; N, 2.2; I, 71.4%).

(d) *Quinoline-2-aldehyde Methochloride*.—*N-Methylquinaldinium tri-iodide* (5.37 g; 0.01 mol) in boiling ethanol (350 ml) was treated with silver nitrate (5.5 g) in water (15 ml) in a nitrogen atmosphere. The mixture was at once cooled to 0 °C, excess sodium chloride added, filtered, and the filtrate evaporated at 40 °C in nitrogen. The residue was reextracted with absolute ethanol, and repetition of the evaporation and extraction process gave, on addition of dry ether, *quinoline-2-aldehyde methochloride* (1 g, 45% yield), crystallizing from chloroform-ether as pale yellow needles, m.p. 148–149 °C (decomp.) (Found: C, 64.0; H, 4.6; N, 6.8%. Calc. for $C_{11}H_{10}ONCl$: C, 63.7; H, 4.8; N, 6.7%). A mixed m.p. with *N-methylquinaldinium chloride* (m.p. 148–149 °C) gave a depression of 25 °C.

The 2, 4-dinitrophenylhydrazones, crystallized from 90% ethanol, had m.p. 245–246 °C (Found: N, 18.2%. Calc. for $C_{11}H_{14}O_4N_2Cl$: N, 18.1%).

(e) *Quinoline-2-aldehyde Methiodide*.—Treatment of the above *methochloride* with sodium iodide in absolute ethanol gave an almost quantitative yield of the *methiodide*, crystallizing from ethanol in dark red prisms, m.p. 177–178 °C (Found: C, 43.95; H, 4.0; N, 5.1%. Calc. for $C_{11}H_{10}ONI$: C, 44.2; H, 3.5; N, 4.7%). Its *phenylhydrazone*, formed readily on addition of phenylhydrazine to a cold ethanolic solution of the aldehyde methiodide, crystallized from methanol-water-ethanol (1:2:4) in red needles, m.p. 244–245 °C (decomp.) (Found: C, 51.9; H, 4.1; N, 11.0%. Calc. for $C_{17}H_{16}N_2I$: C, 52.4; H, 4.1; N, 10.8%).

(f) *Quinoline-2-aldehyde Phenylhydrazone*.—Sublimation of the above phenylhydrazone (0.3 g) at 250–280 °C/0.001 mm gave a sublimate (0.1 g, 53% yield) of quinoline-2-aldehyde phenylhydrazone, crystallizing from ethanol in pale yellow plates, m.p. 203–204 °C, undepressed on admixture with an authentic specimen. Kaufmann and Valette (1913) give m.p. 203–204 °C.

(g) *N-Methyl-2-phenyliminoquinaldinium Iodide*.—Nitrosobenzene (0.65 g) and *N-methylquinaldinium iodide* (1.5 g) were dissolved in boiling ethanol (20 ml) and sodium acetate (0.25 g) added. An immediate dark green colouration appeared, and 30 sec later the product separated (1.2 g). Crystallization from ethanol gave the Schiff's base as bronze coloured leaflets, m.p. 189–190 °C (Found: N, 7.5; I, 33.6%. Calc. for $C_{17}H_{15}N_2I$: N, 7.6; I, 33.9%).

(h) *Hydrolysis of the Schiff's Base*.—The above Schiff's base (0.44 g) was shaken with hydrochloric acid (15 ml; 1.5N) until solution occurred (3 min). Phenylhydrazine (0.13 g) was immediately added; precipitation of the bright red phenylhydrazone began on slight warming and was complete in 30 min. The product was extracted into chloroform, and evaporation of the washed (water) and dried (anhydrous sodium sulphate) extracts gave quinoline-2-aldehyde methiodide phenylhydrazone (0.32 g, 70% yield) as red needles, m.p. 244–245 °C (decomp.). A mixed m.p. with the phenylhydrazone in Section II (e) was undepressed.

(i) *N-Methylquinaldinium Tri-iodide from Quinoline-2-aldehyde Methochloride*.—A solution of quinoline-2-aldehyde methochloride (1.5 g) in 50% aqueous ethanol (10 ml) was treated with cold potassium iodide (10 g) in water (12 ml). The solution rapidly darkened and evaporation *in vacuo* afforded dark brown plates (1.5 g) of *N-methylquinaldinium tri-iodide*, m.p. 139–140 °C, undepressed on admixture with the material in Section II (c).

(j) *N-Methylquinaldinium Picrate*.—(i) Addition of concentrated methanolic lithium picrate to *N-methylquinaldinium tri-iodide* in the same solvent gave *N-methylquinaldinium picrate* crystallizing from methanol as yellow needles, m.p. 139 °C, shrinking at 134 °C (Found: C, 52.9; H, 3.8%. Calc. for $C_{17}H_{14}O_7N_4$: C, 52.9; H, 3.7%). (ii) Prepared from *N-methylquinaldinium iodide* and lithium picrate, the picrate had m.p. 138 °C, shrinking at 135 °C, undepressed on admixture with the material in Section II (j) (i). (iii) *N-Methylquinaldinium tri-iodide* in boiling ethanol was treated with excess hot saturated silver picrate solution. The mixture was boiled for 2 min, filtered hot, the cooled filtrate treated with sodium chloride, and refiltered. Concentration of the filtrate *in vacuo* gave the picrate as needles, m.p. 139 °C sintering at 134–135 °C (Found: C, 52.9; H, 4.0%), undepressed on admixture with the material in Section II (j) (i).

(k) *1, 1', 2'-Trimethylisocyanine Chloride*.—A refluxing solution of *N-methylquinaldinium iodide* (2 g) in ethanol (50 ml) was treated with silver nitrate (2 g; 150% excess) in water (10 ml). After 1.5 hr, excess sodium chloride was added, silver halides filtered off, and the filtrate made just alkaline with potassium hydroxide solution. The yellow precipitate was washed with water and boiled with ethanol (50 ml) in air. The dye (1.05 g, 86% yield) obtained on evaporation was washed (boiling water and ether) and chromatographed on alumina in chloroform solution, the strongly adsorbed blue dye being eluted with chloroform-ethanol (95:5) to give deep blue needles, m.p. 214–216 °C (decomp.) (Found: N, 8.0%. Calc. for $C_{22}H_{21}N_2Cl$: N, 8.0%). Light absorption: A solution of the dye in ethanol (95%) had λ_{max} 5630 Å.

(l) *1, 1'-Dimethylisocyanine Chloride 2'-Carboxylic Acid*.—A solution of silver nitrate (6 g) in water (15 ml) was added to *N-methylquinaldinium tri-iodide* (6 g) in boiling ethanol (350 ml) and the mixture refluxed for 1 hr. After addition of excess sodium chloride, the precipitated silver halides were filtered and the yellow filtrate made just alkaline with potassium hydroxide solution. The brown precipitate A was filtered, and the filtrate concentrated and extracted with chloroform. Evaporation of the dried (sodium sulphate) extracts gave a brown residue B. Both A and B on boiling in ethanolic solution in air gave the blue dye (0.7 g, 33% yield), purified by chromatography in chloroform solution on magnesia to give deep blue needles, m.p. 268–272 °C (decomp.) (Found: C, 69.3; H, 5.1; N, 7.4%. Calc. for $C_{22}H_{19}O_2N_2Cl$: C, 69.7; H, 5.1; N, 7.4%). A mixed m.p. with the material obtained in Section II (k) showed a depression of 46 °C. Light absorption: a 95% ethanolic solution of the dye showed λ_{max} 5630 Å.

(m) *N-Methyl-lepidinium Tri-iodide*.—A solution of *N-methyl-lepidinium iodide* (2.85 g; 0.01 mol) in water (50 ml) was treated gradually with iodine (2.54 g; 0.01 mol) in potassium iodide solution over 30 min with vigorous stirring. Stirring was continued for a further 2 hr, the precipitated solid washed with water and crystallized from ethanol, giving long brown needles (2.8 g, 100% yield based on iodine) of *N-methyl-lepidinium tri-iodide*, m.p. 140 °C (Found: C, 24.7; H, 2.2; N, 2.7%. Calc. for $C_{11}H_{12}NI_3$: C, 24.5; H, 2.2; N, 2.6%).

(n) *N-Methyl-lepidinium Picrate*.—(i) A solution of *N-methyl-lepidinium tri-iodide* in boiling ethanol was treated with excess silver nitrate solution. The cooled colourless solution was filtered, the filtrate treated with excess sodium chloride solution, refiltered, and the filtrate evaporated to dryness *in vacuo*. Extraction with absolute ethanol gave *N-methyl-lepidinium nitrate*, m.p. 169–171 °C (decomp.). It gave a negative test for chloride ion, and a positive test for nitrate ion.

Treatment of the methonitrate with lithium picrate solution gave *N-methyl-lepidinium picrate* as yellow needles from methanol, m.p. 159 °C (decomp.) (Found: C, 53.0; H, 3.6%. Calc. for $C_{17}H_{14}O_7N_4$: C, 52.9; H, 3.6%).

(ii) Treatment of *N-methyl-lepidinium tri-iodide* in boiling methanol with lithium picrate solution gave *N-methyl-lepidinium picrate*, m.p. and mixed m.p. 159 °C (decomp.).

(iii) Reaction of *N-methyl-lepidinium iodide* and excess lithium picrate gave the picrate, m.p. and mixed m.p. 159 °C (decomp.).

(o) *Bis(N-methyl-lepidinium) Octaoidide*.—A vigorously-stirred solution of *N-methyl-lepidinium iodide* (5.7 g; 0.02 mol) in water (175 ml) was treated dropwise at 20 °C over 1 hr with a solution of iodine (16.24 g; 0.065 mol) in potassium iodide. The initially brown precipitate turned black as the addition proceeded. After a further 2 hr stirring, the product was

filtered, washed (water and ether), and shaken with dry ether. The residue (13.1 g, 100% yield based on methiodide) crystallized from chloroform as lustrous black plates of *bis*(*N*-methyl-lepidinium) octaiodide, m.p. 104–104.5 °C (Found: C, 19.3; H, 1.8; N, 2.3; I, 76.0%. Calc. for $C_{11}H_{12}NI_8$: C, 19.8; H, 1.8; N, 2.1; I, 76.3%).

III. ACKNOWLEDGMENTS

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THE SYNTHESIS AND PROPERTIES OF SOME GLYCOSIDES

By M. A. JERMYN*

[Manuscript received April 6, 1955]

Summary

A number of new glycosides and their acetates, principally β -glucosides, have been synthesized and their physical constants are reported. Certain limitations have been found to the application of the modified Helferich synthesis (Jermyn 1954).

I. INTRODUCTION

Investigations into the specificity of the β -glucosidase of *Stachybotrys atra* (Jermyn 1955) required the synthesis of a number of aryl glycosides some of which have not previously been reported. An attempt was made in each case to synthesize them by a technique already described (Jermyn 1954) in which the reaction melt from the Helferich (1933) condensation is crystallized directly from ethanol. For β -glucosides, this method depends on the much smaller solubility of the tetra-*O*-acetyl-aryl- β -glucoside in ethanol than any of the competing reaction products.

II. EXPERIMENTAL

Microanalyses were carried out in the C.S.I.R.O. Microanalytical Laboratory.

The reaction conditions used have already been described in detail (Jermyn 1954). The glycosides were prepared from the *O*-acetates by catalytic deacetylation with sodium in ethanol.

In Table 1 are set out the properties of a number of glycosides and their *O*-acetates which have been synthesized for the first time in the course of this work. The general experimental details of the condensation reaction are summarized with other material in Table 2, but specific details are indicated by footnotes to Table 1.

III. FACTORS INFLUENCING THE HELFERICH REACTION

Many scattered observations on the synthesis of glycosides by the Helferich reaction exist in the literature, but it is difficult to draw any conclusions from them. During the course of work in this laboratory a number of glycosides have been synthesized under nearly standard conditions and the results are set out in Table 2.

It appears that the general conclusion of Helferich and Schmitz-Hillebrecht (1933) that zinc chloride and high temperatures favour the α -anomer and *p*-toluenesulphonic acid and lower temperatures favour the β -anomer is true,

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TABLE I
PHYSICAL PROPERTIES AND ANALYTICAL VALUES FOR SOME NEWLY-SYNTHESIZED GLYCOSIDES

All *O*-acetates recrystallized from ethanol and all glycosides from water unless otherwise indicated. Melting points are uncorrected

Compound	Crystalline Form and M.P. (°C)	[α_D^{20}] (degrees)	Concn. <i>c</i> (%)	Empirical Formula	Analytical Value (%)			
					C	H	N	O
<i>p</i> -Nitrophenyl- α -D-mannoside	White flakes, 174	+144.5	0.2 in H ₂ O	C ₁₂ H ₁₃ NO ₈	f. 47.8 c. 47.8	5.0 5.0	4.7 4.7	
<i>p</i> -Nitrophenyl- α -D-mannoside tetra- <i>O</i> -acetate	White needles, 154	+207	4 in CHCl ₃	C ₂₆ H ₂₂ NO ₁₂	f. 51.2 c. 51.2	4.8 4.9	3.1 3.0	
<i>o</i> -Carbomethoxyphenyl- α -D-glucoside tetra- <i>O</i> -acetate	Glistening white needles, 131-132	+155	4 in CHCl ₃	C ₂₂ H ₂₄ O ₁₂	f. 54.8 c. 54.8	5.5 5.4		
<i>m</i> -Methoxyphenyl- β -D-glucoside*	White powder, 157	-69.8	1 in H ₂ O	C ₁₃ H ₁₅ O ₇	f. 54.4 c. 54.5	6.4 6.3	38.7 39.1	
<i>m</i> -Methoxyphenyl- β -D-glucoside tetra- <i>O</i> -acetate	White needles, 127-128	-19	4 in CHCl ₃	C ₂₇ H ₂₈ O ₁₁	f. 55.7 c. 55.5	5.8 5.8		
<i>p</i> -Iodophenyl- β -D-glucoside	White needles, 180-181	-58	1 in H ₂ O	C ₁₂ H ₁₁ IO ₆	f. 37.7 c. 37.7	4.3 4.3		
<i>p</i> -Iodophenyl- β -D-glucoside tetra- <i>O</i> -acetate	White needles, 143-144	-13.1	4 in CHCl ₃	C ₂₆ H ₂₃ IO ₁₀	f. 43.9 c. 43.7	4.4 4.2	22.8 23.1	
<i>p</i> -Iodophenyl- α -D-glucoside tetra- <i>O</i> -acetate†	White needles, 105-106	+32.4	2 in CHCl ₃	C ₂₆ H ₂₃ IO ₁₀	f. 43.8 c. 43.7	4.2 4.2		
2,4-Di-iodo-6-methylphenyl- β -D-glucoside	White needles from ethanol, 219	-12.5	1 in EtOH	C ₁₃ H ₁₁ I ₂ O ₆	f. 29.9 c. 29.9	3.1 3.1		
2,4-Di-iodo-6-methylphenyl- β -D-glucoside tetra- <i>O</i> -acetate	White needles, 218	-20.2	4 in CHCl ₃	C ₂₇ H ₂₄ I ₂ O ₁₀	f. 36.6 c. 36.6	3.7 3.5	22.9 23.2	

TABLE 1 (Continued)

Compound	Crystalline Form and M.P. (°C)	[α_D^{20}] (degrees)	Concn. c (%)	Empirical Formula	Analytical Value (%)				
					C	H	N	O	I
1-Methyl-2-naphthyl- β -D-glucoside	White needles, 199-201	-64	0.2 in H ₂ O	C ₁₁ H ₂₀ O ₆	f. 63.5 c. 63.7	6.4		30.2 30.0	
1-Methyl-2-naphthyl- β -D-glucoside tetra-O-acetate	White needles, 159-160	-34.6	4 in CHCl ₃	C ₂₁ H ₃₈ O ₁₀	f. 61.5 c. 61.5	5.9 5.8		32.8 32.8	
2,4,6-Tri-iodophenyl- α -D-glucoside tetra-O-acetate†	White needles, 180	+85	2 in CHCl ₃	C ₃₀ H ₃₁ I ₃ O ₁₀	f. 29.8 c. 29.7	2.8 2.6			
o-Iodophenyl- β -D-glucoside	White needles, 156	-48.5	1 in H ₂ O	C ₁₃ H ₁₅ IO ₆	f. 37.4 c. 37.7	4.2 4.0			
o-Iodophenyl- β -D-glucoside tetra-O-acetate	White needles, 154-155	-48.2	4 in CHCl ₃	C ₃₀ H ₃₃ IO ₁₀	f. 44.6 c. 44.6	4.2 4.2			
2-Naphthyl- β -D-glucoside‡	White needles, 183	-88	1 in H ₂ O	C ₁₄ H ₁₉ O ₆	f. 63.0 c. 62.7	6.1 5.9		31.1 31.3	
3-Carboxy-2-naphthyl- β -D-glucoside tetra-O-acetate	Yellow needles from ethyl acetate, 188-189	-60	1.5 in CHCl ₃	C ₂₃ H ₂₆ O ₁₂	f. 57.7 c. 57.9	5.2 5.1			

* The glucoside came down as a gel from all solvents tried. It was obtained as a solid product by slow evaporation of a boiling ethanolic solution.

† Recovered from the mother liquors from which the β -anomer had crystallized.

‡ Attempted deacetylation gave only 2,4,6-tri-iodophenol.

§ The tetra-O-acetate was prepared by Helferich and Schmitz-Hillebrecht (1933) but the free glucoside has not been described.

|| The reactants (2-hydroxy-3-naphthoic acid and β -PAG) had to be heated to 180°C to give a homogeneous melt before addition of catalyst under the conditions indicated in Table 2. No crystalline glucoside could be recovered from attempts to deacetylate the O-acetate by various methods.

TABLE 2

ACETYLATED GLYCOSIDES FROM ACETYLATED SUGARS AND PHENOLS UNDER VARIOUS CONDITIONS
All reaction times are 30 min unless otherwise specified. Some data are from Jermyn (1954)

First Reactant	Second Reactant	Reaction Temp.	Catalyst	Anomer	Yield	Remarks
Phenols :						
<i>o</i> -Methoxy (guaiacol)	Penta- <i>O</i> -acetyl- β -D-glucose	100	I*	—	0	β -PAG recovered almost quantitatively
"	"	140	"	β	37	
<i>m</i> -Methoxy ..	"	100	"	β	29	
<i>p</i> -Methoxy ..	"	100	"	β	33	
2-Methoxy-4-formyl (vanillin)	"	100	"	—	0	
"	"	140	"	—	0	
<i>o</i> -Chloro ..	"	100	"	—	0	
"	"	140	"	β	6	Did not crystallize from EtOH solution of the reaction melt
<i>p</i> -Chloro ..	"	100	"	β	44	
2,4-Dichloro	"	100	"	β	18	Difficult to purify from contaminating β -PAG
<i>o</i> -Methyl ..	"	100	"	β	37	
<i>m</i> -Methyl ..	"	100	"	β	33	
<i>p</i> -Methyl ..	"	100	"	β	43	
2,6-Dimethyl	"	100	"	—	0	
"	"	140	"	β	5	Did not crystallize from EtOH solution of the reaction melt
2- <i>iso</i> Propyl-4-methyl (thymol)	"	100	"	β	18	
<i>o</i> -Carboxy ..	"	100	"	β	37	
<i>p</i> -Carboxy ..	"	100	"	—	0	Excessive tar formed
<i>o</i> -Carboxymethoxy	"	140	"	—	0	β -PAG recovered
"	"	140	II†	$\left\{ \begin{array}{l} \alpha \\ \beta \end{array} \right.$	$\left\{ \begin{array}{l} 16 \\ 2 \end{array} \right.$	
<i>p</i> -Phenyl ..	"	100	I	β	47	
<i>o</i> -Phenyl ..	"	100	"	—	0	
<i>o</i> -Iodo ..	"	120	"	β	16	Did not crystallize from EtOH solution of the reaction melt
<i>p</i> -Iodo ..	"	120	"	$\left\{ \begin{array}{l} \beta \\ \alpha \end{array} \right.$	$\left\{ \begin{array}{l} 48 \\ 2.5 \end{array} \right.$	
2,4-Di-iodo-6-methyl	"	140	I	—	0	β -PAG recovered
"	"	140	II	β	8	

* *p*-Toluenesulphonic acid.

† Zinc chloride.

TABLE 2 (Continued)

First Reactant	Second Reactant	Reaction Temp.	Catalyst	Anomer	Yield	Remarks
2,6-Di-iodo-4-methyl	Penta- <i>O</i> -acetyl- β -D-glucose	140	I	—	0	β -PAG recovered
	"	140	II	—	0	No identifiable product
2,4,6-Tri-iodo	"	140	I	—	0	β -PAG recovered
	"	140	II	α	5.5	
1-Naphthol ..	"	100	I	β	40	
2-Naphthols :	"	"	"	"	"	
Unsubstituted	"	130	"	β	39	
6-Bromo- ..	"	100	"	β	21	
1-Bromo- ..	"	100	"	—	—	β -PAG recovered
		140	"	β	5	Difficult to purify from contaminating β -PAG
1-Methyl- ..	"	100	"	β	19	
1-Formyl- ..	"	100	"	—	0	β -PAG recovered
3-Carboxy-	"	120	"	β	17	
Phenol	Octa- <i>O</i> -acetyl- β -maltose	100	"	β	47	
"	"	140 (2 hr)	II	α	35	
"	Octa- <i>O</i> -acetyl- β -lactose	100	I	β	51	
"	"	140 (2 hr)	II	α	42	
<i>p</i> -Nitrophenol ..	Penta- <i>O</i> -acetyl- β -D-glucose	160	"	{ β α }	31	
" ..	Penta- <i>O</i> -acetyl- β -D-mannose	160	"		36	
" ..	Penta- <i>O</i> -acetyl- β -D-galactose	160	"	β	55	
" ..	Octa- <i>O</i> -acetyl- α -cellobiose	160	"	β	25	
" ..	Octa- <i>O</i> -acetyl- β -maltose	160	"	β	18	
" ..	Octa- <i>O</i> -acetyl- β -lactose	160	"	β	31	

except when strongly acid or *ortho*-substituted phenols are employed. Many *ortho*-substituted phenols fail to react in the presence of *p*-toluenesulphonic acid at 100 °C and some fail to react or give very low yields at 140 °C. The nitro-compounds (Jermyn 1954) and polyiodo-compounds react only in the presence of zinc chloride at the higher temperatures to give mixtures of the α - and β -anomers depending on the reactants and temperature.

It has already been concluded (Jermyn 1954) that the proportions of the products in the high temperature reactions of the acid phenols were determined

by a rapid initial reaction and changed very slowly thereafter. The nature of the main product does not appear to follow directly from the configuration of the sugar acetate ; thus, for the condensation with *p*-nitrophenol, under identical conditions penta-*O*-acetyl- β -D-mannose gives a high yield of the α -anomer and octa-*O*-acetyl- α -cellobiose gives the β -anomer as the sole isolable product.

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THE SYNTHESIS OF ANGUSTIFOLIONOL

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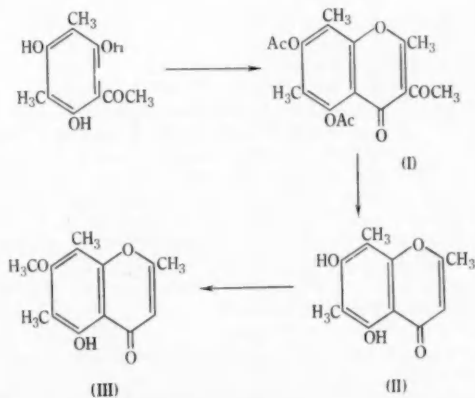
[Manuscript received February 23, 1955]

Summary

Angustifolionol (5-hydroxy-7-methoxy-2,6,8-trimethylchromone) has been synthesized by three different methods.

I. METHOD A

Angustifolionol is a natural product and was shown by degradation reactions to be 5-hydroxy-7-methoxy-2,6,8-trimethylchromone (Birch, Elliott, and Penfold 1954). It was thought desirable to confirm this formula by synthesis, following the process developed by Schmid and Bolleter (1950) and Mukerjee, Seshadri, and Varadarajan (1953) for eugenitin (5-hydroxy-7-methoxy-2,6-dimethylchromone).



Dimethylphloroglucinol was prepared by the method of Robertson and Whalley (1951) using zinc cyanide instead of anhydrous hydrogen cyanide without appreciable reduction in yield. It was converted to dimethylphloracetophenone by the Hoesch reaction (e.g. Campbell and Coppinger 1951). The low yields from the hydrolysis of the intermediate imine were improved by working under nitrogen. The chromone (I) was readily obtained, but in

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therefore that the starting material must be II, which is known to be readily methylated to form angustifolionol (methods A and C). Its m.p. 284–286 °C is quite close to that of eugenitol 276–278 °C. How this trimethylchromone was obtained in the method intended for the synthesis of eugenitol (IV) (below) is not clear and the question is under consideration.

III. METHOD C

*iso*Eugenitol (V) appeared to be a convenient starting-material for II and III and the extra *C*-methyl group has been introduced in two different ways. Condensation with hexamethylenetetramine in glacial acetic acid solution produced a good yield of the 6-aldehyde VI, which was reduced using a palladium-charcoal catalyst to give II, and methylated by potassium carbonate and methyl iodide in acetone to angustifolionol (III).

The nuclear methylation of *isoeugenitol* (V) is a more direct and convenient method. It has been carried out using methyl iodide and sodium methoxide in absolute methanol. The product was a mixture; the major, more soluble fraction was angustifolionol (III). The minor, less soluble fraction was found to be 5,7-dihydroxy-2,6,8-trimethylchromone (II). This is another case where there is evidence of *C*-methylation prior to *O*-methylation of an hydroxyl *para* to the pyrone carbonyl group. An earlier instance was reported by Jain and Seshadri (1954).

IV. EXPERIMENTAL

(a) *Method A*.—Dimethylphloracetophenone (1 g), fused sodium acetate (1.2 g), and acetic anhydride (10 c.c.) were heated in a bath at 150 °C for 85 hr. The mixture was poured into water, extracted with ether, and distilled; the distillate, b.p. 195–210 °C/0.1 mm, was treated with 5N hydrochloric acid (9 c.c.) for 45 min, the 5,7-diacetoxy-3-acetyl-2,6,8-trimethylchromone was removed by filtration and crystallized from ethanol, m.p. 169 °C (Found: C, 62.8; H, 5.6%. Calc. for $C_{18}H_{18}O_7$: C, 62.4; H, 5.2%). Hydrolysis: (i) the compound above (0.6 g) was taken up in methanol containing sodium (0.122 g) and kept at 10 °C for 14 hr and 20 °C for 3 hr. After acidifying to congo paper and ether extraction the 7-acetoxy-3-acetyl-5-hydroxy-2,6,8-trimethylchromone (60 mg) was crystallized from ethanol, m.p. 239 °C (Found: C, 63.1; H, 5.5%. Calc. for $C_{18}H_{18}O_8$: C, 63.1; H, 5.3%). It gave a green colour with alcoholic ferric chloride. This substance was refluxed with methyl iodide and potassium carbonate (0.22 g) in acetone for 18 hr. Worked up as usual, 3-acetyl-5-hydroxy-7-methoxy-2,6,8-trimethylchromone was obtained as pale yellow needles from ethanol, m.p. 125 °C (Found: C, 65.1; H, 5.9%. Calc. for $C_{18}H_{18}O_8$: C, 65.2; H, 5.8%). It gave a deep blue-green colour with ferric chloride.

This compound was heated with 5N hydrochloric acid, extracted with ether, the ether washed with potassium hydroxide solution (5%), and then evaporated. The small crystalline residue, m.p. 95 °C, was not depressed in m.p. by angustifolionol and gave a blue-green colour with alcoholic ferric chloride; there was insufficient for further purification.

The triacetylchromone (I) (0.8 g) was refluxed for 2 hr with sodium carbonate solution (10%) and gave crude 5,7-dihydroxy-2,6,8-trimethylchromone (0.3 g), m.p. 279 °C, which was directly methylated with excess diazomethane at 0 °C in ether-methanol. Sublimation of the product at 150–160 °C/0.2 mm and crystallization from ethanol gave crystals, m.p. 119 °C, which was not depressed on admixture with angustifolionol, m.p. 119 °C (Found: C, 66.6; H, 6.2%. Calc. for $C_{18}H_{18}O_8$: C, 66.7; H, 6.0%).

(b) *Method C*.—(i) 6-Formyl-5,7-dihydroxy-2,8-dimethylchromone. A solution of 5,7-dihydroxy-2,8-dimethylchromone (1 g) in glacial acetic acid (25 c.c.) was heated with hexamine (4 g) on the steam-bath for 3 hr. A pale yellow solid started separating from the clear mixture

after about 1 hr and the separation appeared to be complete in 3 hr. The mixture was then treated with boiling hydrochloric acid (20 c.c.; 1:1), the heating continued for another 0.5 hr, the mixture was then diluted with water, cooled, and the precipitated solid filtered off. It crystallized from a mixture of ethanol and chloroform as pale yellow flat needles (0.7 g), m.p. 189–190 °C (Found: C, 61.3; H, 4.2%. Calc. for $C_{12}H_{10}O_2$: C, 61.5; H, 4.3%).

It was sparingly soluble in ethanol and acetone, but soluble in chloroform and glacial acetic acid. It gave a reddish violet colour with ferric chloride in alcoholic solution. Its yellow dinitrophenylhydrazine crystallized from pyridine as fibrous needles which did not melt below 300 °C.

(ii) *5,7-Dihydroxy-2,6,8-trimethylchromone (II)*. A solution of the above aldehyde (0.5 g) in glacial acetic acid (35 c.c.) was shaken with palladium charcoal (10%; 1.5 g) in an atmosphere of hydrogen. The hydrogen (2 mole) was absorbed in about 8 hr. The solution was then filtered from the catalyst which was washed with boiling acetic acid (3 × 5 c.c.). The combined filtrate and washings were diluted with water when a colourless product separated. It was filtered off and crystallized twice from ethanol yielding 5,7-dihydroxy-2,6,8-trimethylchromone as colourless rectangular rods and prisms (0.3 g), m.p. 284–286 °C. It was soluble in cold aqueous sodium carbonate solution and gave a bluish green colour with alcoholic ferric chloride (Found: C, 65.1; H, 5.5%. Calc. for $C_{12}H_{12}O_4$: C, 65.5; H, 5.5%).

The diacetate, obtained by the acetic anhydride-pyridine method, crystallized from ethyl acetate as colourless needles, m.p. 199–201 °C.

(c) *Angustifolionol (III)*.—(i) *By Partial Methylation of II*. The above dihydroxy compound (0.1 g) was partially methylated by refluxing it with methyl iodide (1 c.c.) and potassium carbonate (2 g) in acetone (50 c.c.) for 1.5 hr. The product crystallized from dilute alcohol as almost colourless, long flat needles and rectangular prisms, m.p. 117–118 °C. It gave a deep bluish green colour with alcoholic ferric chloride.

(ii) *By Nuclear Methylation of isoEugenitol (V)*. An ice-cold solution of 5,7-dihydroxy-2,8-dimethylchromone (1 g) in methanol (50 c.c.) containing sodium methoxide (from 1.4 g Na) was treated with methyl iodide (5 c.c.). The mixture was heated under reflux for 4 hr. Most of the methanol was then removed under reduced pressure and the residue was treated with ice and dilute hydrochloric acid. The yellowish precipitate thus obtained was filtered off, washed with water and then fractionally crystallized from ethanol. Angustifolionol was obtained in the more soluble fraction and it crystallized from dilute ethanol as almost colourless long flat needles and rectangular prisms (0.4 g), m.p. 117–118 °C alone or when mixed with the sample described in Section (c) (i) above.

The fraction, sparingly soluble in ethanol (0.15 g), m.p. 284–286 °C, was soluble in aqueous sodium hydroxide solution. It was identical with 2,6,8-trimethyl-5,7-dihydroxychromone (II) described earlier.

Methylation of *isoeugenitol* by boiling with methyl iodide-potassium carbonate in acetone medium yielded only the *O*-methyl ether, *isoeugenitin*, and no nuclear methylation took place.

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COLOURING MATTERS OF AUSTRALIAN PLANTS

V. HAEMOCORIN : THE CHEMISTRY OF THE AGLYCONE

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[Manuscript received April 5, 1955]

Summary

Oxidation of the aglycone dimethyl ether B gives a cyclic anhydride isomeric with that previously obtained from dimethyl ether A. The chemical properties and absorption spectra of the two anhydrides and their derivatives suggest that they are dimethoxyphenylnaphthalic anhydrides with the methoxyl groups attached to the naphthalene ring system. Further degradation of the anhydrides eventually gives diphenyl-2,3,4-tricarboxylic acid. This is proved by decarboxylation to diphenyl and by the formation of an anilide phenylimide identical with a synthetic specimen. These results indicate that the aglycone is a dihydroxymethoxyphenylperinaphthenone, and further support is given by a study of model hydroxyperinaphthenones.

I. INTRODUCTION

In Part IV of this series (Cooke and Segal 1955), the aglycone from haemocorin was shown to contain a cyclic enolic α -diketone structure. Evidence was also given for the presence of an extended tautomeric enolone system involving more than one ring. Further support for these conclusions is now given by the oxidation of the aglycone dimethyl ether B to a yellow cyclic anhydride, isomeric with that previously obtained from dimethyl ether A.

II. THE NATURE OF THE ANHYDRIDES

The two anhydrides are very similar in properties. Both are yellow and dissolve slowly in hot dilute alkali and are regenerated on acidification. However, the initially precipitated acids are colourless and, if rapidly recovered, are converted by diazomethane to isomeric colourless esters. Attempts to crystallize the acids from organic solvents result in dehydration to the anhydrides.

These properties suggest that the compounds are polycyclic aromatic anhydrides and more specific evidence of their structures is obtained from a detailed study of the light absorption of the anhydrides and the derived dimethyl esters.

The infra-red absorption spectra of the anhydrides show two significant features. Firstly, the characteristic double carbonyl bands show the unique

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combination of low frequency and very small separation. A survey of published values for a wide variety of anhydrides suggests that this feature is characteristic of 1,8-naphthalic type anhydrides (Cooke 1955). Secondly, the infra-red spectrum shows bands in the regions characteristic of the unsubstituted phenyl group (*c.* 700 and 750 cm^{-1}). Similar bands are also present in the spectrum of the aglycone. These results and the molecular composition $\text{C}_{20}\text{H}_{14}\text{O}_5$ suggest that the compounds are dimethoxyphenylnaphthalic anhydrides.

Further support is given by the ultraviolet spectra of the anhydrides, which show some resemblance to those recorded by Hirshberg and Jones (1949) for some phenylnaphthalene-1,2- and -2,3-dicarboxylic anhydrides in inert solvents. However, it has been shown by Hirshberg, Lavie, and Bergmann

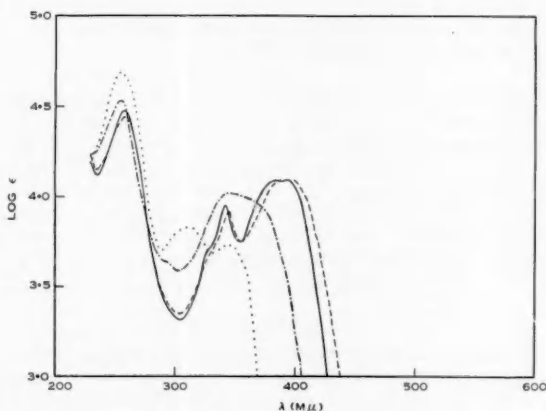


Fig. 1.—Absorption spectra.

- Anhydride B in ethanol.
- Anhydride B in dioxan.
- · - · - 4-Methoxy-2-phenylnaphthalic anhydride in ethanol.
- Dimethyl ester from anhydride A in dioxan.

(1951) that the spectra of these compounds change in alcohols because of reaction with the solvent. The anhydrides from haemocorin give the same spectra in both kinds of solvent (Fig. 1). The greater stability is quite consistent with the 1,8-naphthalic anhydride structure.

The ultraviolet spectra of the dimethyl esters derived from the anhydrides are of the phenylnaphthalene type (Fig. 1). They strongly resemble the spectra of phenylnaphthalene derivatives reported by Shrecker and Hartwell (1953) and by Dannenberg (1954).

Further confirmation of the structural type is obtained by direct comparison with a model compound, 4-methoxy-2-phenylnaphthalic anhydride, which was prepared for the purpose (see below). The infra-red absorption spectrum of this compound shows striking similarities to that of anhydride A from haemocorin.

Infra-red Absorption Spectra (in "Nujol")

Anhydride A: 1764, 1727, 1575, 1488, 1340, 1238, 1181, 1148, 1048, 1033, 1019, 970, 879, 848, 813, 779, 768, 717, 709, 689.

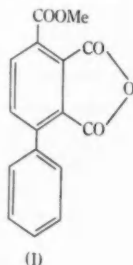
4-Methoxy-2-

phenylnaph- 1762, 1724, 1621, 1584, 1502, 1291, 1234, 1199, 1189, 1176,
thalic an- 1163, 1117, 1089, 1044, 1011, 977, 865, 846, 820, 794,
hydride 766, 752, 710, 706, 700, 679 cm^{-1} .

The ultraviolet spectrum (Fig. 1) is also similar and shows the same stability in ethanol. The lighter colour and weaker long-wave absorption, as shown in the curve, are probably due to both the phenyl and methoxyl groups being attached to the same ring. In the anhydrides derived from haemocerin the substituents must be attached to different rings and this results in greater total conjugation.

III. OTHER DEGRADATION PRODUCTS

The conclusions of the preceding section were confirmed by further degradation of the anhydrides. In one experiment the aqueous mother liquors from the oxidation of dimethyl ether A (see Part IV loc. cit.) yielded a product which was reoxidized with excess hot alkaline permanganate. The resulting gummy acid gave diphenyl when heated with soda-lime.



Further degradation of each of the pure isomeric anhydrides also gave intractable acid gums. Esterification of these with diazomethane also gave uncrystallizable products which readily gave the same solid derivative, $\text{C}_{27}\text{H}_{18}\text{N}_2\text{O}_9$, when heated with aniline. This compound appeared to be a mono-anilide phenylimide of a diphenyltricarboxylic acid and was identical with the compound prepared by the action of aniline on the known diphenyl-2,3,4-tricarboxylic acid derivative I (Alder and Schumacher 1951).

The two specimens showed no depression of melting point when mixed, and had the same infra-red absorption spectrum.

IV. THE NATURE OF THE AGLYCONE MODEL COMPOUNDS

The accumulated evidence suggests that the aglycone is a dihydroxy-methoxyphenylperinaphthenone. Very little is known of the chemistry of hydroxyperinaphthenones and no compounds resembling the aglycone have

been investigated. Although tautomerism of the *perinaphthene* structure was postulated by Klyne and Robinson (1938) and there has been considerable

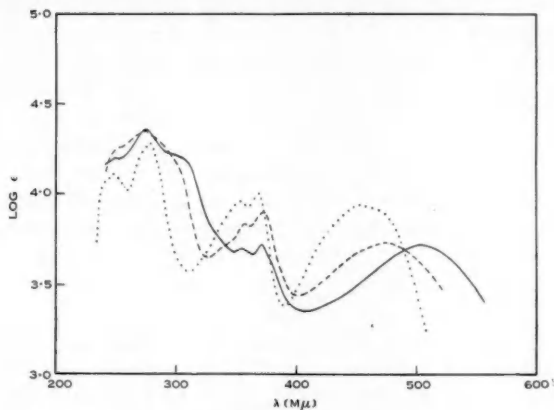


Fig. 2.—Absorption spectra.

- Haemocorin aglycone in dioxan.
- - - Monomethyl ether A in dioxan.
- Monomethyl ether B in dioxan.

recent interest in the subject (Badger, Carruthers, and Cook 1949; Boekelheide and Goldman 1954), no examples of reversible transformation have been recorded,

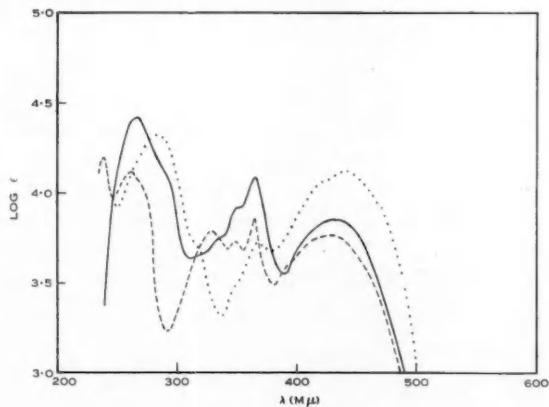


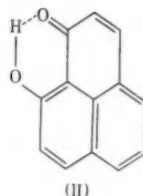
Fig. 3.—Absorption spectra.

- Aglycone diacetate in dioxan.
- - - 2-Hydroxyperinaphthenone in dioxan.
- 6-Methoxy-4-phenylperinaphthenone in ethanol.

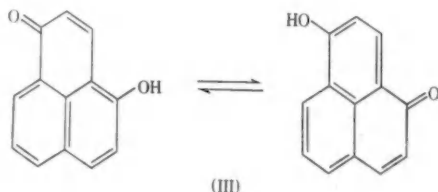
and the possible tautomeric nature of suitable hydroxyperinaphthenones has not been discussed.

Very few hydroxyperinaphthenones have been described and their absorption spectra have not been recorded. However, Cromwell, Capps, and Palmer (1951) have studied the light absorption of some 2-aminoperinaphthenone-1 derivatives and their curves are similar to those obtained for the aglycone and its mono-methyl ethers (Fig. 2).

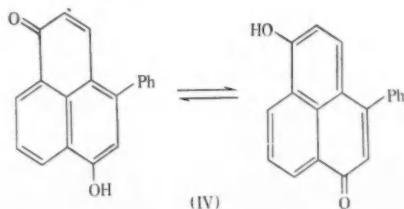
The known 2-hydroxyperinaphthenone-1 was therefore prepared and its spectrum is now found to be of the same type. It is recorded with the aglycone diacetate absorption curve in Figure 3.



Of the possible tautomeric hydroxyperinaphthenones only one, 9-hydroxyperinaphthenone-1 (II), has been described. Suitably substituted derivatives of this might be expected to give two isomeric ethers. However, Koelsch and Anthes (1941) were unable to methylate or acylate II, and it is now confirmed that the compound cannot be methylated under conditions which are effective for the aglycone.



As representatives of the other possible tautomeric structures the compounds III and IV have now been prepared.

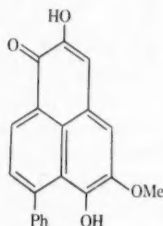


It is realized that one form of the free compounds may be much more stable than the other, and III and IV are arbitrarily named 4-hydroxyperinaphthenone-1 and 6-hydroxy-4-phenylperinaphthenone-1 respectively.

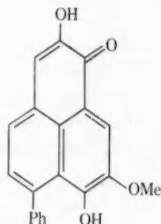
As expected, each of these compounds gives two isomeric methyl ethers, and their properties are generally similar to those of the aglycone and its derivatives. The compounds III and IV are deeply coloured and have high melting points. They dissolve in aqueous alkalis to give strongly coloured and intensely fluorescent solutions. The absorption spectra (Fig. 3 and Section V) show resemblances to those of the aglycone and its derivatives, although the bands characteristic of the enolic α -diketone structure are of course absent.

The structures of the isomeric ethers derived from III and IV were determined by oxidation. Thus the ethers from III gave respectively 2- and 4-methoxynaphthalic anhydride. Similarly one of the ethers from IV gave a product which must be 4-methoxy-2-phenylnaphthalic anhydride. One of the ethers obtained from III is evidently identical with the 4-methoxyperinaphthenone prepared unambiguously by Badger, Carruthers, and Cook (1949).

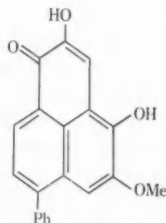
All these results suggest that the structure of the aglycone must belong to one of the following types V, VI, and VII. As a lactol ester, $C_{22}H_{18}O_7$,



(V)



(VI)



(VII)

was only obtained from one of the aglycone dimethyl ethers, the suggested contiguous arrangement of the second pair of oxygen substituents is based on the following observations. The infra-red spectrum of the aglycone in carbon tetrachloride shows two hydroxyl bands, one at 3542 cm^{-1} (sharp) and the other at 3380 cm^{-1} (broader). The second is assigned to the enolic α -diketone group in one ring, while the first is consistent with a guaiacol type of grouping. These two hydroxyl bands also agree respectively with the single hydroxyl bands given by the aglycone monomethyl ethers.

Finally, the methyl ethers of compounds III and IV and the aglycone methyl ethers are readily demethylated by mild acid treatment. Under the same conditions the original methoxyl group of the aglycone is unaffected. It is presumably not conjugated in the same way with the carbonyl group.

V. EXPERIMENTAL

Unless otherwise stated, all melting points are corrected and were observed in Pyrex capillaries. Light petroleum refers to a fraction of boiling range $40\text{--}60^\circ\text{C}$. Ultraviolet spectra were measured with a Hilger Uvispek photoelectric spectrophotometer. Microanalyses are by Dr. K. W. Zimmermann and assistants.

(a) *Oxidation of the Aglycone Dimethyl Ether B.*—The ether was oxidized with potassium permanganate in acetone essentially as described for dimethyl ether A (Cooke and Segal 1955).

The anhydride was recovered in the usual way and it separated from ethanol in fine yellow needles, m.p. 157 °C (Found: C, 71.5; H, 4.3; MeO, 18.4%. Calc. for $C_{26}H_{14}O_5$: C, 71.8; H, 4.2; 2 × MeO, 18.6%); light absorption in ethanol (95%): λ_{\max} (m μ) 395, 345, 257.5; log ϵ_{\max} 4.09, 3.92, 4.44. The infra-red spectrum showed the characteristic carbonyl bands at 1767 and 1733 cm^{-1} .

Other properties of this compound were also similar to those of the isomeric anhydride obtained from dimethyl ether A. The unstable acid obtained by acidification of a solution in alkali was readily converted by diazomethane to a colourless *dimethyl ester* which separated from methanol as fine needles, m.p. 125.5–126 °C (Found: C, 69.6; H, 5.1; MeO, 31.7%. Calc. for $C_{22}H_{20}O_6$: C, 69.5; H, 5.2; 4 × MeO, 32.6%); light absorption in dioxan: λ_{\max} (m μ) 352.5, 321.5, 252.5; log ϵ_{\max} 3.86, 3.96, 4.51. Hydrolysis of this ester regenerated the anhydride.

No compound isomeric with the lactol ester $C_{22}H_{18}O_7$ (Cooke and Segal 1955) was obtained by oxidation of dimethyl ether B.

(b) *Degradation of Dimethyl Ether A to Diphenyl*.—After oxidation of the ether with permanganate in acetone and isolation of the two crystalline products as previously described (Cooke and Segal 1955), the aqueous mother liquors were continuously extracted with ether. The recovered gum (containing a few crystals) was dissolved in aqueous sodium hydroxide (5%) and the solution was heated on the water-bath while aqueous potassium permanganate solution was added in portions, with shaking, until the colour was no longer rapidly discharged. An excess of permanganate was then added and heating was continued for 1 hr, after which some of the reagent still remained. Sodium sulphite and hydrochloric acid were added and the clear solution was extracted continuously with ether. Evaporation of the dried extract again gave a gum from which a few crystals separated on standing. The whole product was mixed with soda-lime and copper bronze and the mixture was heated in a stream of nitrogen. The crystalline distillate, which had the odour of diphenyl, was crystallized several times from aqueous methanol (charcoal) to give pearly leaflets, m.p. 69–70 °C not depressed by authentic diphenyl (Found: C, 93.7; H, 6.7%. Calc. for $C_{12}H_{10}$: C, 93.5; H, 6.5%).

(c) *Further Oxidation of Anhydride B*.—The pure anhydride (30 mg; m.p. 157 °C) was dissolved in hot aqueous sodium hydroxide (1%; 30 c.c.) and powdered potassium permanganate (100 mg) was added. The mixture was heated in boiling water for 2 hr. After acidification and reduction of manganese compounds with sulphur dioxide, the clear solution was saturated with salt to precipitate a crystalline solid. This *acid* was crystallized several times from water but could not be purified satisfactorily. The melting point appeared to depend on the conditions of drying the sample and on the rate of heating. After prolonged drying one sample had m.p. 185 °C (Found: C, 60.5; H, 4.1; MeO, 8.3%). As the material still contained methoxyl it was hydrolysed with boiling aqueous sodium hydroxide to give an acid which, after crystallization from water, had m.p. 259 °C and contained no methoxyl group. As this was difficult to purify, it was esterified with diazomethane and the resulting *ester* was purified by chromatography in benzene over silica gel, and by sublimation in a high vacuum. It crystallized from methanol in prisms, m.p. 123–124 °C (Found: C, 63.3; H, 4.6; MeO, 23.3%; mol. wt. (Rast), 379. Calc. for $C_{21}H_{18}O_4$: C, 63.0; H, 4.8; 3 × MeO, 23.2%; mol. wt., 398). This compound presumably contains all the skeletal carbon atoms of the original anhydride and is formed by fission of the methoxylated ring. It was not further investigated.

The mother liquor from the initial oxidation product above was extracted continuously with ether and the recovered oil was dissolved in aqueous sodium hydroxide (5%) and heated on the water-bath with successive additions of potassium permanganate until an excess persisted for $\frac{1}{2}$ hr. The product, recovered in the same way, was an acid gum which could not be crystallized. It was esterified with diazomethane and the product was purified by chromatography on silica gel and by distillation in a high vacuum. However, it could not be crystallized and was therefore boiled with excess aniline for $\frac{1}{2}$ hr. The cooled mixture was treated with dilute hydrochloric acid and the light yellow solid was further purified by washing with boiling ethanol. It was finally crystallized from benzene to give the *anilide phenylimide of diphenyl-2,3,4-tricarboxylic acid* as cream microscopic crystals, m.p. 252–253 °C (Found: C, 77.8; H, 4.7; O, 11.6; N, 6.7%. Calc. for $C_{22}H_{18}N_2O_5$: C, 77.5; H, 4.3; O, 11.5; N, 6.7%).

This substance was identical (mixed m.p. and infra-red spectrum) with a specimen prepared by the action of aniline on 4-methoxycarbonyldiphenyl-2,3-dicarboxylic anhydride (Alder and Schumacher 1951). It was also obtained from the products of similar oxidative degradations of the pure anhydride A.

(d) *Preparation of 4-Hydroxyperinaphthenone-1*.—This compound was prepared substantially as described by Koelsch and Anthes (1941) for the 9-hydroxy isomer, but without isolation of the intermediate styryl ketone, and using double the proportion of aluminium chloride. The cinnamoyl chloride was first condensed with α -naphthyl methyl ether by gradual addition of half the aluminium chloride to the ice cold benzene solution. After standing about $\frac{1}{2}$ hr, the remainder of the aluminium chloride was added and the mixture was boiled for $\frac{1}{2}$ to 1 hr. When the mixture was decomposed in the usual way with ice and hydrochloric acid, a sparingly soluble solid was obtained. This was washed with hot ethanol, sublimed in a high vacuum, and the 4-hydroxy-perinaphthenone crystallized from ethanol or glacial acetic acid as orange-red microscopic needles, m.p. about 260°C decomp. (uncorr.) (Found: C, 79.0; H, 4.4%. Calc. for $C_{18}H_{10}O_2$: C, 79.6; H, 4.1%). This compound dissolved readily in aqueous alkalis, giving yellow solutions with intense yellow-green fluorescence in daylight or ultraviolet light.

(e) *4-Methoxy- and 7-Methoxyperinaphthenone-1*.—The crude 4-hydroxyperinaphthenone was methylated by refluxing with dimethyl sulphate and potassium carbonate in acetone. The crude mixture of ethers was dissolved in benzene and separated by chromatography over silica gel. The first fractions yielded a yellow crystalline product which was sublimed in a high vacuum and crystallized from benzene-light petroleum to give 7-methoxyperinaphthenone as yellow needles, m.p. 132–133°C (Found: C, 80.3; H, 4.5%. Calc. for $C_{14}H_{10}O_2$: C, 80.0; H, 4.8%); light absorption in ethanol: λ_{\max} (m μ) 412.5, 342.5, 260; $\log \epsilon_{\max}$ 4.14, 3.72, 4.48. The structure was checked by oxidation with permanganate in acetone to a product which was evidently 4-methoxynaphthalic anhydride. It formed pale yellow needles from glacial acetic acid, m.p. 256–257°C (uncorr.). Lit. gives m.p. 255–257°C (Found: C, 68.4; H, 3.6%. Calc. for $C_{13}H_8O_4$: C, 68.4; H, 3.5%).

The last fractions from the silica column gave orange crystals which were purified by vacuum sublimation and crystallization from benzene-light petroleum to give 4-methoxyperinaphthenone as orange needles, m.p. 142–143°C. Badger, Carruthers, and Cook (1949) report m.p. 142–143°C (Found: C, 79.8; H, 4.8%. Calc. for $C_{14}H_{10}O_2$: C, 80.0; H, 4.8%); light absorption in ethanol: λ_{\max} (m μ) 432, 317.5, 262.5; $\log \epsilon_{\max}$ 4.17, 3.68, 4.46. Oxidation of this isomer gave a product which was evidently 2-methoxynaphthalic anhydride. It separated from glacial acetic acid in almost colourless needles, m.p. 252–253°C (uncorr.). Lit. gives 255–257°C (Found: C, 68.3; H, 3.8%. Calc. for $C_{13}H_8O_4$: C, 68.4; H, 3.5%).

(f) *β -(4-Methoxy-1-naphthyl)cinnamic Acid*.—4-Methoxy-1-benzoylnaphthalene (24 g), ethyl bromoacetate (10 c.c.), benzene (25 c.c.), toluene (25 c.c.), and zinc (6 g) were heated together with a trace of iodine until the reaction started, and the mixture was then boiled for 6 hr. Dilute hydrochloric acid was added to the cooled solution and the organic layer was separated, washed, and evaporated. Ethanol was added to the residue and much unchanged ketone separated. This was collected and the filtrate was hydrolysed by boiling with alcoholic potassium hydroxide. The ethanol was then evaporated and water was added to precipitate the remaining ketone, which was collected. Acidification of the filtrate gave a sticky resinous precipitate which solidified when rubbed with ethanol. The acid was crystallized from ethanol with the aid of charcoal. It formed almost colourless diamond-shaped prisms, m.p. 228–229°C decomp. (uncorr.). Yield 2 g (Found: C, 78.4; H, 5.3%. Calc. for $C_{20}H_{14}O_3$: C, 78.8; H, 5.3%).

(g) *6-Methoxy-3-phenylperinaphthenone-1*.—The above acid (1.1 g) was dissolved in conc. sulphuric acid (15 c.c.) and the mixture was allowed to stand in a stoppered flask for 2 hr. The deep crimson solution gradually deposited crystals. The mixture was shaken with water and the solid was filtered, washed with aqueous sodium hydroxide, then with water, and was dried. Yield 0.96 g. The 6-methoxy-3-phenylperinaphthenone crystallized from benzene-light petroleum as small orange prisms, m.p. 167–168°C (Found: C, 84.1; H, 5.1; MeO, 10.5%. Calc. for $C_{20}H_{14}O_3$: C, 83.9; H, 4.9; MeO, 10.8%); light absorption in ethanol: λ_{\max} (m μ) 440, 357.5, 325, 265; $\log \epsilon_{\max}$ 4.08, 3.66, 3.90, 4.26.

(h) *6-Hydroxy-4-phenylperinaphthenone-1*.—The above ether (0.25 g), ethanol (20 c.c.), water (20 c.c.), and conc. sulphuric acid (10 c.c.) were refluxed for 6 hr. A deep red crystalline oxonium salt separated slowly during the reaction and this was eventually collected and dissolved in excess dilute aqueous sodium hydroxide. Acidification with hydrochloric acid then precipitated the free *6-hydroxy-4-phenylperinaphthenone* which crystallized from acetone in small red plates with a bronze lustre, m.p. 269 °C decomp. (Found: C, 83.4; H, 4.7%. Calc. for $C_{19}H_{12}O_2$: C, 83.8; H, 4.4%); light absorption in dioxan: λ_{\max} (m μ) 435, 355, 272.5; log ϵ_{\max} 3.97, 3.53, 4.25. The compound dissolves readily in aqueous alkalis to give a magenta solution with a strong orange-red fluorescence in daylight and ultraviolet light.

(i) *6-Methoxy-4-phenylperinaphthenone-1*.—The above hydroxyphenylperinaphthenone was methylated with dimethyl sulphate and potassium carbonate in acetone. The mixture of ethers was crystallized from benzene-light petroleum to give *6-methoxy-4-phenylperinaphthenone* as the less soluble component. It formed clusters of silky orange needles, m.p. 214–215 °C (uncorr.) (Found: C, 83.5; H, 4.9%. Calc. for $C_{20}H_{14}O_2$: C, 83.9; H, 4.9%); light absorption in ethanol: λ_{\max} (m μ) 440, 367.5, 282.5; log ϵ_{\max} 4.12, 3.71, 4.32.

Oxidation of this ether with permanganate in acetone gave a neutral product which must be *4-methoxy-2-phenylnaphthalic anhydride*. It separated from glacial acetic acid in pale yellow needles, m.p. 195–196 °C (uncorr.). If allowed to resolidify, it then melted at 205–206 °C (Found: C, 74.7; H, 4.1%. Calc. for $C_{18}H_{12}O_4$: C, 75.0; H, 4.0%); light absorption in ethanol: λ_{\max} (m μ) 357.6, 345, 255; log ϵ_{\max} 3.99, 4.02, 4.53 (italicized values represent inflexion).

(j) *Attempted Hydrolysis of the Aglycone*.—The aglycone was heated with alcoholic sulphuric acid as under Section V (h). The compound was recovered unchanged, as shown by acetylation to the diacetate (m.p., mixed m.p., and analysis). However, the dimethyl ether A was readily hydrolysed, even by weaker acid, and some aglycone was obtained from the mixture.

VI. ACKNOWLEDGMENTS

The authors are indebted to Mr. L. J. Webb and Mr. J. G. Tracey, C.S.I.R.O., for continued supplies of the plant material. Dr. J. B. Willis, C.S.I.R.O., established the identity of the anilide samples by infra-red analysis. The other infra-red spectra were measured by Mr. R. L. Werner, New South Wales University of Technology.

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THE CHEMICAL CONSTITUENTS OF AUSTRALIAN *FLINDERSIA* SPECIES

VIII. THE STRUCTURE OF MACULINE

By R. J. GELL,* THE LATE G. K. HUGHES,* and E. RITCHIE*

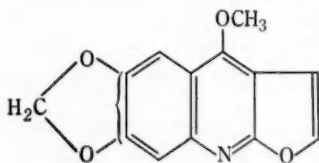
[Manuscript received February 24, 1955]

Summary

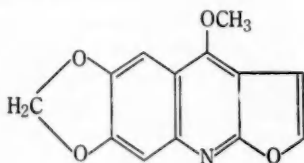
Maculine is shown by degradation to be 6,7-methylenedioxydictamnine (II).

I. INTRODUCTION

In Part V of this series (Brown *et al.* 1954), the isolation of maculine from the bark of *Flindersia maculosa* Lindl. together with a preliminary examination of the alkaloid was described. Maculine analysed for $C_{13}H_9O_4N$, contained one methoxyl group, and gave a positive Labat methylenedioxy test. It was isomerized to isomaculine on heating with methyl iodide, and had an ultraviolet absorption spectrum similar to those of kokusagine and skimmianine. This evidence suggested that maculine was a methylenedioxydictamnine (I).



(I)



(II)

As kokusagine, which is different from maculine, has already been shown to be 7,8-methylenedioxydictamnine (Narahashi, Ohta, and Terasaka 1954), this leaves only the 5,6- and 6,7-positions possible for the methylenedioxy group in maculine. In order to distinguish between these alternate structures, maculine was hydrogenolysed and demethylated to the 3-ethyl-2,4-dihydroxyquinoline, after the method used for the degradation of evolatine (Gell, Hughes, and Ritchie 1955). 3-Ethyl-6,7-methylenedioxy-2,4-dihydroxyquinoline was synthesized from 3,4-methylenedioxyaniline and diethyl ethyl malonate in boiling diphenyl ether. This product was identical with that obtained from maculine as shown by direct comparison (mixed melting points and X-ray powder photographs) of the dihydroxyquinolines themselves and their acetyl derivatives. Maculine is therefore 6,7-methylenedioxydictamnine (II).

* Department of Organic Chemistry, University of Sydney.

II. EXPERIMENTAL

Melting points are uncorrected. Powder photographs were taken in a 19 cm X-ray Powder Camera, using CuK α radiation. Microanalyses are by Miss B. Stevenson, University of Sydney.

(a) *Degradation of Maculine*.—Maculine (0.18 g) was dissolved in ethanol (20 ml) and hydrogenolyzed at room temperature and pressure in the presence of Adams's catalyst. The product was demethylated by heating under reflux with hydrochloric acid (5N; 15 ml) for 30 min. The precipitate which separated on cooling to 0 °C was dissolved in aqueous sodium hydroxide (charcoal) and the product precipitated with acetic acid. The product (0.04 g) crystallized from ethanol in colourless plates, m.p. 300–303 °C (Found: C, 61.6; H, 4.8%. Calc. for C₁₂H₁₁O₄N: C, 61.8; H, 4.7%).

(b) *Synthesis of 3-Ethyl-6,7-methylenedioxy-2,4-dihydroxyquinoline*.—Diethyl ethyl malonate (1.88 g) and 3,4-methylenedioxyaniline (1.40 g) in diphenyl ether (20 ml) were heated under reflux for 45 min. The mixture was cooled, hexane (50 ml) added, and the precipitate collected. The crude material was dissolved in aqueous sodium hydroxide (charcoal) and the product precipitated with acetic acid. The product (0.70 g, 30% yield) crystallized from ethanol in colourless plates, m.p. 300–303 °C (Found: C, 61.9; H, 5.0; N, 5.7%. Calc. for C₁₃H₁₁O₄N: C, 61.8; H, 4.7; N, 6.0%). The mixed m.p. with the substance obtained in (a) was not depressed. The X-ray powder photographs of the two substances were identical.

The acetyl derivative (presumably the 4-acetoxy-) was prepared by heating the dihydroxyquinoline (0.4 g) with acetic anhydride (5.0 ml) and pyridine (1 drop) on the water-bath for 2 hr. The product crystallized from ethanol in colourless needles, m.p. 292–295 °C (Found: C, 61.0; H, 4.8; N, 5.3%. Calc. for C₁₄H₁₃O₅N: C, 61.1; H, 4.7; N, 5.1%). By the same method, an acetyl derivative was prepared from the substance obtained from maculine. It crystallized from ethanol in colourless needles, m.p. 292–295 °C, undepressed on admixture with the above. The X-ray powder photographs of the two substances were identical.

III. ACKNOWLEDGMENT

The authors wish to thank Mr. H. C. Freeman, University of Sydney, for the X-ray powder photographs.

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STUDIES OF WAXES

IX. THE NORMAL ALCOHOLS OF WOOL WAX

By K. E. MURRAY* and R. SCHOENFELD*

[Manuscript received December 21, 1954]

Summary

Seven normal alcohols have been isolated from the unsaponifiable part of wool wax and identified as *n*-octadecanol, *n*-eicosanol, *n*-docosanol, *n*-tetracosanol, *n*-hexacosanol, *n*-octacosanol, and *n*-triacontanol.

I. INTRODUCTION

In a previous investigation (Murray and Schoenfeld 1952) of the aliphatic alcohols present in the unsaponifiable fraction of wool wax, the isolation and identification of 10 branched-chain alcohols belonging to the *iso*- and *anteiso*-series were described. This work did not reveal the presence of normal alcohols, although there was the possibility that they were present as minor constituents, distilling as their acetates in the intermediate fractions between the plateau corresponding to the acetates of the individual *iso*- and *anteiso*-alcohols. This was contrary to the findings of Tiedt and Truter (1952), who considered them the most abundant of the aliphatic alcohols. Weitkamp (1945) found the normal members to be relatively minor constituents of the acids of wool wax and it seemed possible that an analogous composition might hold for the alcohols. This has now been found to be the case and the present paper describes the isolation of a series of seven normal alcohols of even carbon number from C_{18} to C_{30} , occurring in relatively small amounts. It seemed that Tiedt and Truter's qualitative separation of the wax alcohols with urea adducts could have given a wrong impression of the proportion of normal alcohols present.

The separation of normal and branched alcohols of the same carbon number by distillation having proved difficult it was decided to effect a preliminary concentration of the normal alcohols by adduct formation with urea. This has been greatly simplified by the use of a recent method of Bowman and Weitkamp (1952) which involves urea adduct formation of the esters of the mixed alcohols with a branched-chain acid. The esters of the branched alcohols with branched acids do not form adducts, or do so to a much smaller extent than the like esters of the normal alcohols. Bowman and Weitkamp's method was applied, using *isobutyric* esters, to the aliphatic alcohols which had first been separated from cyclic alcohols by adduct formation with urea. The normal

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alcohols were then separated by amplified distillation of their acetates (Weitkamp 1947; Murray and Schoenfeld 1951) and final purification especially of the higher alcohols C_{26} , C_{28} , and C_{30} was effected by repeated recrystallization.

II. EXPERIMENTAL

Microanalyses were carried out in the C.S.I.R.O. Microanalytical Laboratory.

(a) *Isolation of n-Alcohols.*—The starting material for this work as for a previous investigation (Murray and Schoenfeld 1952) was a wax obtained from Merino wool. The saponification of the wax and the acetylation of the unsaponifiable fraction have been described in this earlier work. The procedure by which the pure alcohols were obtained consisted of the following stages:

- (i) Separation of the acetylated aliphatic alcohols from the acetylated unsaponifiable fraction in the form of urea adducts.
- (ii) Hydrolysis of the aliphatic acetates from (i) and, after esterification of the alcohols to isobutyrate with isobutryl chloride, separation of the esters of branched and normal alcohols with urea.
- (iii) Liberation of the normal alcohols from the separated isobutyrate, followed by conversion to their acetates. Fractional distillation of these acetates followed by further purification of each molecular species by amplified distillation.
- (iv) Recrystallization of the alcohols recovered from (iii) to constant melting point.

Details are as follows: (i) In general, the method was similar to that of Zimmerschied *et al.* (1950) and was performed in batches, a typical run being: The acetylated unsaponifiable fraction (250 g) dissolved in light petroleum (b.p. 90–110 °C; 1.5 l.) was shaken for 1 hr with powdered urea (600 g) and methanol (250 ml). Excess urea and adducts were filtered off and washed with light petroleum. The filtrates were concentrated to 1.5 l. and shaken with urea and methanol as above. A third treatment was found to yield little or no adduct and was omitted in subsequent runs. The adducts were decomposed by warm water and the liberated acetates extracted with ether. A total of 144 g of adduct-forming acetates was obtained from 1550 g of the acetylated unsaponifiable fraction. This gave 125 g of alcohols on saponification. Besides eliminating the cyclic alcohols it is probable that the foregoing treatment achieved a partial separation of normal and branched alcohols.

(ii) The above alcohols were converted to their isobutyric esters by dissolving them in benzene (1 l.) at 70 °C, adding isobutryl chloride (75 g) dropwise, refluxing for 1 hr, and distilling off benzene and excess chloride. The residue was dissolved in light petroleum (b.p. 60–80 °C; 500 ml) and passed through a column of neutral alumina to remove polar impurities. The light petroleum eluate yielded 142 g of almost colourless isobutyrate. These were then treated with urea to form the urea adducts of the esters of the *n*-alcohols. The procedure followed that described above with proportionate amounts of solvent, urea, and methanol. A trial experiment had shown that a single urea treatment (involving two shakings) was not sufficient to separate the esters of normal and branched alcohols effectively for the reasons given subsequently in Section II (a) (iii). Consequently, the adducted esters from the first treatment were retreated in a similar manner and this was repeated. The adducted esters (50 g) thus obtained were saponified and the alcohols acetylated by heating with a large excess of acetic anhydride at 100 °C for 6 hr, the excess anhydride distilled off, and the last traces removed azeotropically with light petroleum (b.p. 80–100 °C). The acetates weighed 48.5 g and had a saponification number of 121.

(iii) An amplified distillation of 5 g of these acetates was made in the general manner described in previous papers (Murray and Schoenfeld 1951, 1953) to determine whether separation of the *n*-alcohols had been complete by the above urea separation. As with all subsequent distillations in this work it was performed in a 10 ft spinning band column (Murray 1951) at 1.00 mm pressure. Plotting the saponification numbers of the collected fractions (Fig. 1) shows four distribution peaks which correspond to the boiling points of the acetates of the C_{26} , C_{28} , C_{24} , and C_{22} normal alcohols. The fractions near these peaks (shown shaded) yielded alcohols with the crystalline appearance of normal alcohols, and melting points of 65.0–65.2, 69.5–69.7, and 74.8–75.0 °C, which are close to those of pure *n*-eicosanol, *n*-docosanol, and *n*-tetracosanol respectively (Table 1).

However, the alcohol from the C_{26} peak fractions melted at $73.4\text{--}73.8^\circ\text{C}$ approximately 5°C below that of pure *n*-hexacosanol. This low melting point was probably due to contamination with the corresponding *iso*-alcohol the boiling point of the acetate of which lies close to that of the *n*-acetate. The presence of C_{25} and C_{27} alcohols is suggested from the incomplete separation of the C_{24} and C_{26} fractions and the C_{26} and a small peak corresponding to C_{28} (Fig. 1). Support was given for the presence of higher branched acetates when it was found that the *isobutyrate*s of pure C_{20} *iso*- and C_{27} *anteiso*-alcohols formed small amounts of urea adducts when added to a saturated solution of urea in methanol. It was concluded from the above evidence that the urea treatment (ii) had effectively separated normal and branched alcohols up to a chain length of C_{24} , but higher branched acetates were present, even though in small amounts in the mixture of acetates from treatment (ii).

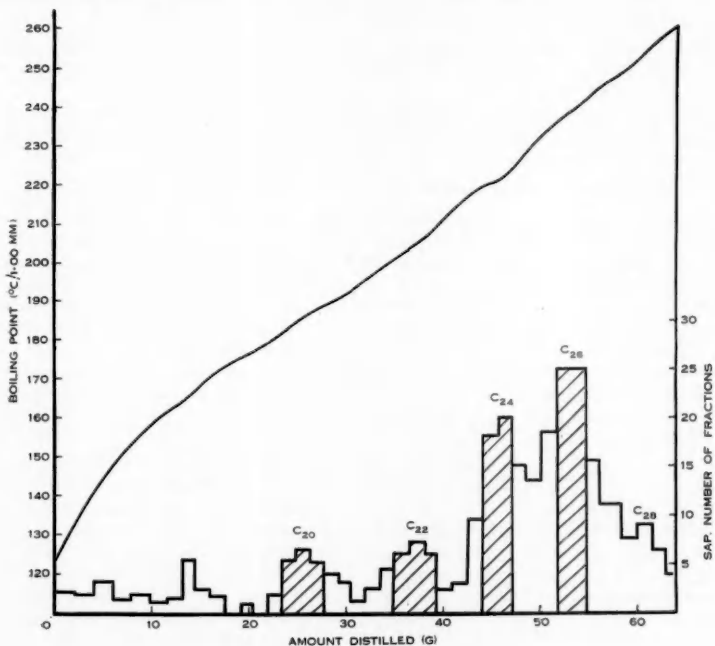


Fig. 1.—Trial amplified distillation.

Rather than submit the main bulk of material to further urea treatments of the *isobutyrate*s it was decided to remove the branched chain impurities by amplified distillation and crystallization. Therefore, the residue of the acetates (43.5 g) was fractionally distilled at 1.00 mm employing as chaser a mineral oil (20 g), which was a distillation residue boiling higher than 270°C at 1 mm. Nineteen fractions covering the range $161\text{--}270^\circ\text{C}$ were collected and then divided into groups according to the following chain lengths: 1, $C_{18}+C_{20}$ (3.47 g); 2, C_{22} (5.13 g); 3, C_{24} (4.66 g); 4, C_{26} (10.09 g); 5, $C_{28}+C_{30}$ (8.64 g). An intermediate fraction between C_{24} and C_{26} was rejected. Each of these collective fractions was then submitted in the above order to amplified distillation at 1.00 mm, using predistilled mineral oil fractions of the appropriate range, the residue of each distillation being added to the charge of the next. The technique of amplified distillation effectively separates chain lengths differing by two carbons even when they are present in small amounts (Weitkamp 1947) and this is well illustrated by Figure 2, which

TABLE I
ALCOHOLS

Alcohol	Melting Point (°C)		Boiling Point of Acetate (°C/1 mm)	Oxygen Analysis		Long Crystal Spacings			
						Present Work		Francis, Collins, and Piper (1937)	
	Literature	Found		Found	Calc.	A Form	B Form	A Form	B Form
n-Octadecanol ..	57.98*	58.0-58.1	166	6.1	5.9	50.3	41.3	50†	41.35
n-Eicosanol ..	65.5	65.4-65.5	184	5.4	5.4	—	45.3	—	45.5†
n-Docosanol ..	70.8	70.5-70.7	201	4.8	4.9	—	49.9	—	50.0
n-Tetracosanol ..	75.3	75.0-75.1	217	4.6	4.5	—	54.0	—	54.25
n-Hexacosanol ..	79.2	78.9-79.0	232	4.3	4.2	—	58.0	—	58.0
n-Octacosanol ..	82.6	82.2-82.3	245	3.8	3.9	—	62.2	—	62.3
n-Triacontanol ..	86.5	85.2-85.5	258	3.9	3.6	81.0	66.6	81.2†	66.4

* Freezing point.

† Calculated value.

shows the separation of the C_{18} and C_{30} acetates in the collective fraction 1. From each of the five amplified distillations only those fractions which boiled within $\pm 1-3^\circ\text{C}$ of the temperature at the distribution peaks were chosen for recovery of the alcohols for identification. However, the C_{28} and C_{30} peak fractions were first reacylated and separately submitted to a second amplified distillation. The alcohols were recovered from the saponified peak fractions by distilling off the solvent used for the saponification ("Cellosolve"-xylene) under vacuum, dissolving the residue in light petroleum free from aromatics (b.p. $60-80^\circ\text{C}$) and chromatographing at 45°C on alumina (Brockmann activity II). The amplifying oil was eluted by light petroleum and the alcohols by benzene.

(iv) The seven alcohols recovered were crystallized to constant melting point. For the C_{18} , C_{20} , C_{22} , C_{24} , and C_{26} members this required from two to six crystallizations from ethyl acetate. Evidently the C_{28} and C_{30} alcohols contained larger amounts of branched-chain impurities. C_{28} required 12 crystallizations from ethyl acetate and finally from benzene. C_{30} was recrystallized 17 times from ethyl acetate, benzene, and finally from toluene.

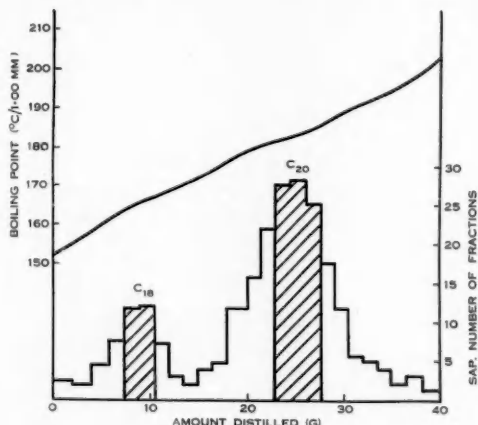


Fig. 2.—Amplified distillation of fraction 1.

(b) *Search for C_{16} and C_{32} Alcohols.*—Figure 2 shows clearly the absence of alcohols below C_{18} . However, acting on the possibility that shorter chain lengths had been lost during the urea treatments of the isobutyrate, an amplified distillation was made on the acetates derived from the non-adducting isobutyrate of the third urea treatment. No *n*-hexadecanol was found and the search was abandoned.

The distillation of the main bulk of the acetates left a considerable residue which, assuming that none of the chaser had distilled over, comprised 22% of the charge. Although this residue had been heated to above 300°C at the end of the distillation, and could therefore be expected to be largely decomposed, it was examined for the presence of the C_{32} *n*-alcohol by dissolving in light petroleum, chromatographing on alumina to remove any polar matter formed by decomposition, followed by amplified distillation at 0.5 mm . Only a small amount of an alcohol (0.08 g) was recovered from a small peak, which corresponded roughly with the b.p. of the acetate of *n*-dotriacontanol (257°C). However, after three recrystallizations from toluene it had m.p. $80.0-80.5^\circ\text{C}$ far below that of pure *n*-dotriacontanol ($89.3-89.5^\circ\text{C}$, see Piper, Chibnall, and Williams 1934), and more in keeping with the expected m.p. of the C_{32} *iso*-alcohol. It had the appearance of a mixture and its identification was not attempted.

(c) *Characterization and Identification of the Alcohols.*—The seven alcohols isolated, which form a series, have been characterized by m.p., long crystal spacing, the b.p. of the acetate, and

by micro-oxygen analysis (Table 1). Five of the alcohols C_{20} to C_{28} isolated in sufficient amount were oxidized to the corresponding acids which were characterized by m.p. and long crystal spacing (Table 2). Both alcohols and acids crystallized in flat rhombs characteristic of long chain alcohols and acids.

(i) *Oxidation to Acids.* The method, using chromium trioxide in acetic acid, followed that of Pollard, Chibnall, and Piper (1931), except the purification of the crude acid from unchanged alcohol was effected by extraction of a solution of the potassium salt in 50% aqueous alcohol with warm light petroleum. The recovered acids were crystallized twice from ethyl acetate and the C_{28} acid was again recrystallized from acetone.

(ii) *Melting Points.* These were determined on melted and resolidified samples in 1 mm capillary tubes, using a fully immersed Anschütz thermometer. The heating bath was provided with rapid stirring and an optical system which magnified the sample and eliminated errors due to parallax. The temperature of the liquid-bath could be held within 0.1°C indefinitely. The C_{20} and C_{28} alcohols melted within 0.1°C , but the accuracy of calibration did not warrant reporting closer than 0.1°C . The m.p.'s of the alcohols isolated are compared in Table 1 with the data of Francis, Collins, and Piper (1937) for the *n*-alcohols. All agree well except perhaps C_{30} , our

TABLE 2
DERIVED ACIDS

Acid	Melting Point ($^\circ\text{C}$)		Long Crystal Spacings			
			Present Work		Francis and Piper (1939)	
	Literature	Found	<i>B</i> Form	<i>C</i> Form	<i>B</i> Form	<i>C</i> Form
<i>n</i> -Eicosanoic ..	75.35	75.0-75.2	48.6	—	48.45	—
<i>n</i> -Docosanoic ..	79.95	79.6-79.7	53.2	48.2	52.9	48.3
<i>n</i> -Tetracosanoic ..	84.15	83.9-84.0	57.7	—	57.75	—
<i>n</i> -Hexacosanoic ..	87.7	87.3-87.5	62.3	56.4	62.2	56.25
<i>n</i> -Octacosanoic ..	90.9	90.4-90.6	—	60.9	—	61.05

value being 1°C low. However, this is reduced to 0.5°C when it is considered that their value for C_{20} is high in relation to the rest of the series. A smooth curve drawn through their values for the C_{24} to C_{34} alcohols suggests that 86.0°C would be a more consistent value. The m.p.'s of the C_{18} and C_{20} alcohols agree with data quoted by Ralston (1948), and the m.p.'s of the derived acids with those of Francis and Piper (1939). Melting points of the C_{18} and C_{30} alcohols were undepressed when mixed with authentic samples of *n*-octadecanol and *n*-triacontanol respectively.

(iii) *Long Crystal Spacings.* These were made by the technique of Francis and Piper (1939). The rocking angle was 25° , collimator aperture 0.6 mm, specimen-film distance 80 mm, and $\lambda = 1.54 \text{ \AA}$ ($\text{CuK}\alpha$ radiation). The spacings found for the alcohols agree closely with those determined by Francis, Collins, and Piper (1937) (Table 1), while those for the acids agree with the data of Francis and Piper (1939) for the *n*-acids (Table 2).

One criterion of purity specified by Piper, Chibnall, and Williams (1934) for long-chain alcohols and acids is that the maximum possible number of orders of reflexion should be evident. This is $n+2$, where n is the number of carbon atoms, and was clearly observed for all the alcohols and acids. A feature of the photographed reflexion patterns is being commented on in a separate paper (Fridrichsons 1955). Piper, Chibnall, and Williams also state that *n*-alcohols and acids when pure crystallize in a single form, *B* for the alcohols and *B* or *C* for the acids depending on the solvent. Five of the alcohols isolated in this work (C_{20} to C_{28}) crystallized in the *B* form and on this basis could be regarded as being of high purity. The most likely impurity in the C_{30} alcohol is the C_{30} *iso*-alcohol but there was no X-ray evidence for other chain lengths.

(iv) *Boiling Points of the Acetates.* As in previous work (Murray and Schoenfeld 1952), these were taken as the temperature of the distribution peak of the acetates in their final amplified distillation. It is noted that they are 2–3 °C higher than those for the corresponding acetylated *iso*-alcohols. The values for the C_{18} and C_{20} members agree with those for the C_{18} and C_{20} *n*-acetates (Murray and Schoenfeld 1951).

III. DISCUSSION

No evidence has been found in this work for normal alcohols below C_{18} . This agrees with the findings of Tiedt and Truter (1952) who however accepted the evidence of Drummond and Baker (1929) for the presence of hexadecanol. In our previous paper a reason was given why Drummond and Baker's identification of hexadecanol is unacceptable. Knol (1954) in a recent review also dismissed their evidence for the same reason.

Tiedt and Truter (1952) state that they found no evidence for the presence of normal alcohols above hexacosanol, although from closer examination of their evidence it appears that higher homologues could be contained in their C_{26} fraction. The reasons are: (i) The wide melting range of their C_{26} alcohol suggests a mixture and straddles the melting point of pure *n*-hexacosanol (79.2 °C, Francis, Collips, and Piper 1937). (ii) The melting point of their C_{26} acetate (63.0 °C) is considerably higher than that of *n*-hexacosyl acetate (60.0–60.1 °C, Piper, Chibnall, and Williams (1934); 60.3–60.4 °C as determined in this Laboratory), and Piper, Chibnall, and Williams have stated that mixed *n*-acetates have melting points determined by the mean molecular weight. For these reasons and the lack of further proof of chain length by long crystal spacings we regard Tiedt and Truter's proof of identification of hexacosanol as inadequate.

In view of the many operations involved in this work in the separation of the individual alcohols an accurate figure for the percentage of normal alcohols in the unsaponifiable fraction is not possible but an overall estimate is 2 to 3 per cent. This value is consistent with the fact that there was no positive evidence of their presence in our previous fractional distillations (Murray and Schoenfeld 1952) because of the greater bulk of the branched alcohols. The relative amounts of the alcohols is probably in the decreasing order C_{26} , C_{24} , C_{28} , C_{22} , C_{30} , C_{20} , C_{18} , the ratio between C_{20} and C_{18} being approximately 20:1.

Previously we had recognized 22.5 per cent. of aliphatic alcohols in our unsaponifiable fraction. This may now be divided into diols previously determined 1.5 per cent., normal alcohols 2–3 per cent., branched alcohols (*iso*- and *anteiso*- in approximately equal amounts) 18–19 per cent. The ratio between normal and branched alcohols is roughly that found by Weitkamp for normal and branched acids of wool wax. As previously noted for the branched alcohols the normal alcohols have a longer average chain length than the normal acids.

IV. ACKNOWLEDGMENTS

The authors are grateful to Dr. A. W. Weitkamp for suggesting the use of his urea separation, and to Dr. J. Fridrichsons of the Chemical Physics Section of this Division for the determination of long crystal spacings.

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STUDIES OF WAXES

X. THE DIOLS OF CARNAUBA WAX

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Summary

Four α - ω -diols have been isolated from the unsaponifiable fraction of carnauba wax and identified as *n*-docosane-1,22-diol, *n*-tetracosane-1,24-diol, *n*-hexacosane-1,26-diol, and *n*-octacosane-1,28-diol.

I. INTRODUCTION

Stürcke (1884) reported the isolation of a glycol, m.p. 103.5 °C, from carnauba wax, and formulated it as $C_{25}H_{50}(OH)_2$. The presence of this glycol then remained unnoticed until the present authors in an earlier paper (Murray and Schoenfeld 1951) showed that a series of at least three glycols was present, but the amounts then isolated were too small for adequate identification. Saponification of the wax is now found to yield four α - ω -diols identified as *n*-docosane-1,22-diol, *n*-tetracosane-1,24-diol, *n*-hexacosane-1,26-diol, and *n*-octacosane-1,28-diol.

α - ω -Diols have not previously been recognized as constituents of the common waxes. Musgrave, Stark, and Spring (1952), however, have recorded their occurrence in an extract from the flowers of Spanish broom (*Spartium junceum* L.).

II. EXPERIMENTAL

Microanalyses were carried out in the C.S.I.R.O. Microanalytical Laboratory.

(a) *Isolation of the Diols.*—(i) *Saponification of the Wax and Separation of the Unsaponifiable Material.* Carnauba wax ("Flores No. 1"; 250 g) was refluxed for 20 hr with KOH (50 g) in ethanol (97%; 1 l.) and light petroleum (b.p. 90–110 °C; 500 ml). Hot water (600 ml) was then added, the aqueous alcoholic layer drawn off, and the petrol layer containing the bulk of the unsaponifiable material washed free of potassium soaps with 5 lots of hot ethanol (50%). After the evaporation of the light petroleum 104.3 g of unsaponifiable material remained (fraction 1).

The aqueous alcoholic layer and the washings mentioned above, containing the potassium salts and the balance of the alcohols, were warmed to 55 °C and a solution of calcium chloride ($CaCl_2 \cdot 6H_2O$; 110 g) stirred in. After heating on the steam-bath for 8 hr, when most of the alcohol evaporated, the precipitate of calcium soaps had become granular, and was easily filtered off. The soaps were dried thoroughly (3 days in vacuum at 50 °C) and extracted with ether in a large Soxhlet. After 40 hr, 33.5 g of unsaponifiable matter had been extracted (fraction 2). The soaps were then powdered and further extracted for 120 hr, when the material was exhausted. A further 5.2 g of unsaponifiable material (fraction 3) was obtained in this period. This melted above 90 °C and was considered to be mainly diols. The total yield of unsaponifiable material was 143.0 g or 57.2% of the wax.

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(ii) *Chromatographic Separation of the Crude Diols.* The unsaponifiable material was chromatographed on alumina (Brockmann activity II) at 50°C as follows: Fractions 1 and 2 were combined, dissolved in benzene, and chromatographed on 690 g of alumina. The column was first eluted with benzene (3500 ml) and then with benzene-ethanol (1:1; 2500 ml). The material recovered from the benzene-ethanol eluate (16.0 g) was from previous experience considered to contain the diols, together with monoalcohols not completely eluted by benzene. It was combined with fraction 3 (total 21.2 g) and carefully rechromatographed on a smaller column (210 g alumina). The following fractions were collected:

Fraction	Eluant	Vol. (ml)	Wt. (g)	M.p. (°C)
1	C ₆ H ₆	1500	11.4	83-84.5
2	"	500	1.4	90-92
3	C ₆ H ₆ -EtOH 200:1	500	2.5	91-92.5
4	C ₆ H ₆ -EtOH 1:1	1000	5.6	91-92.5
5	" " "	1000	0.1	—

99% of the material was recovered. From the m.p. the diols appeared to be in fractions 2, 3, 4, and 5, but from its lower melting range and its mobility on alumina fraction 2 may have contained monoalcohols so that fractions 3, 4, and 5 were chosen for further investigation.

(iii) *Amplified Distillation of the Acetylated Diols.* Fractions 3, 4, and 5 were combined and 6.11 g of the mixture was acetylated in the manner previously described for the normal alcohols of wool wax (Murray and Schoenfeld 1955). The acetates melted at 61.5-62°C and had a saponification equivalent of 264.

The acetates (7.12 g) were distilled with a mineral oil (72 g) at 1.00 mm, using a 10-ft spinning band column (Murray 1951). When the head temperature reached 264°C the pressure was reduced to 0.50 mm. Forty-five fractions (c. 5 g each) were collected and their saponification values determined and plotted in the manner previously described (Murray and Schoenfeld 1953). The results are shown in Figure 1. Four prominent peaks are in evidence with maxima at temperatures of 229, 243, 257 (at 1.00 mm), and 258°C (at 0.50 mm). The diols were isolated from the respective saponified fractions (shown shaded) as follows: The solvents used for saponification were distilled off *in vacuo*, the residue taken up in hot ethyl acetate, and the solution washed with water. The ethyl acetate was distilled off and the residue chromatographed in light petroleum on 10 times its weight of alumina at 50°C. The alumina column was washed with light petroleum-benzene (1:1) to remove the amplifying oil, and the diol was then eluted with benzene-ethanol (1:1). The undistilled portion from the amplified distillation was saponified and treated as above to give a higher diols fraction. All diols were crystallized twice from a benzene-acetone mixture.

(b) *Characterization and Identification of the Diols.*—The four isolated diols have been characterized by their m.p.'s, long crystal spacings, and the m.p.'s of their diacetates. These properties, particularly the crystal spacings, taken with the microanalyses and the boiling points of their diacetates (from Fig. 1) clearly establish that they belong to a homologous series in which the members differ by two carbon atoms. The certain identification of the main diol as *n*-tetracosane-1,24-diol has been made by comparison of the diol, its diacetate, the derived diacid, and its dimethyl ester with synthetic samples. By the evidence of homology given above the remaining diols are then *n*-docosane-1,22-diol, *n*-hexacosane-1,26-diol, and *n*-octacosane-1,28-diol.

(i) *Synthetic α - ω -C₂₄ Diol, Diacetate, Diacid, and Dimethyl Ester.* A sample of dimethyl tetracosane-1,24-dioate (m.p. 75.2-75.4°C) of high purity was supplied by Dr. S. F. Birch of the Anglo-Iranian Oil Co. Ltd., London. It had been prepared by the addition of hydrobromic acid to undecylenic acid, treatment of the ω -bromo-compound with potassium cyanide, hydrolysis of the nitrile to the dicarboxylic acid, and electrolysis of the half-ester.

This dimethyl ester was saponified to tetracosane-1,24-dioic acid. After recrystallization from acetone, this compound appeared as large brittle plates which melted at 128.0-128.2°C (Shiina (1939) records 126.9-127.1°C). Its long crystal spacing was 25.6 Å both for pressed and melted specimens. This value agrees closely with an interpolated value of 25.7 Å from the results of Normand, Ross, and Henderson (1926) for the C₂₂ and C₂₆ α - ω -diacids.

Tetracosane-1,24-diol was prepared from the dimethyl ester by reduction with lithium aluminium hydride in ether. It was purified by chromatography on alumina and was finally crystallized from benzene-acetone (see Table 1 for characteristics). The C_{24} diacetate was prepared in the conventional manner. Like the diacetates of the natural diols it crystallized from acetone in large lustrous plates.

(ii) *Oxidation of the Natural C_{24} Diol to the Diacid.* The diol (300 mg) in acetic acid (20 ml) was treated with chromium trioxide (750 mg) in acetic acid (10 ml) at 60–70°C. After 30 min the mixture was poured into water and the crude acid extracted with chloroform. The chloroform solution was extracted with excess KOH in 20% aqueous ethanol, the suspension of potassium

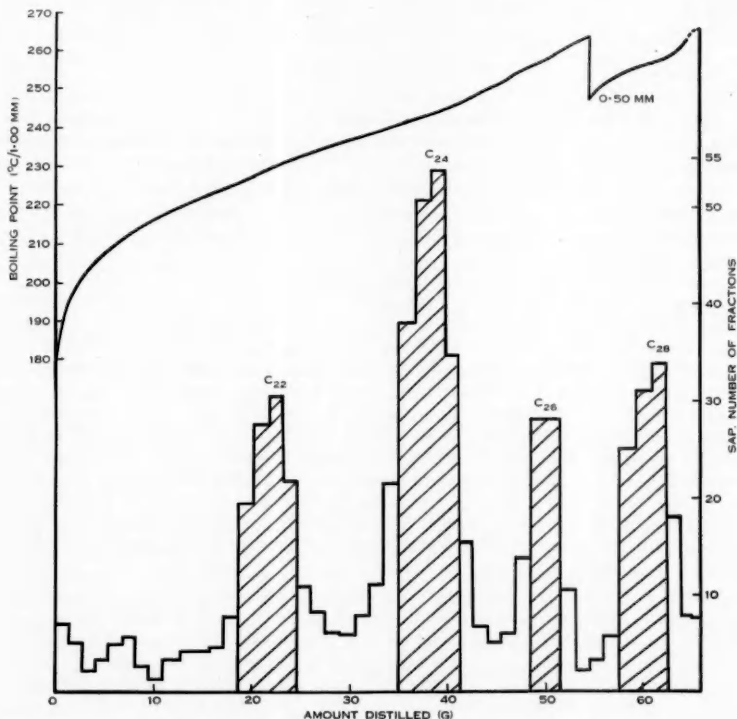


Fig. 1.—Amplified distillation of the acetylated diols.

salts drawn off, and acidified. The liberated acid was extracted by chloroform, and melted at 121.9–122.3°C. It was further purified by conversion to its dimethyl ester which was then chromatographed on neutral alumina (3 g). The light petroleum eluate gave 270 mg of the diester which, when crystallized from acetone, melted at 74.6–74.8°C. On hydrolysis this gave the diacid which after two crystallizations from toluene melted at 127.2–127.5°C.

(iii) *Melting Points.* These were determined as described in a previous paper (Murray and Schoenfeld 1955). Table 1 gives the melting points of the four diols isolated and their diacetates, together with those of the synthetic C_{24} diol and diacetate. The literature contains very few data for comparison. The m.p. of the natural C_{22} diol agrees with the values recorded for

TABLE I
CHARACTERISTICS OF DIOLS AND DIACETATES

Diol	Melting Point (°C)		Long Crystal Spacings		Microanalysis (oxygen %)		Diacetates		
							Melting Point (°C)	Boiling Point (°C/1 mm)	Micro-Acetyl
	Observed	Literature	A Form	C Form	Found	Calc.			
<i>n</i> -Docosane-1,22-diol ..	105.6-105.7	105.3-105.5* 105†	30.3	21.6	9.5	9.3	68.3-68.4	229	Found 19.7 Calc. 20.2
<i>n</i> -Tetracosane-1,24-diol ..	108.4-108.6	—	32.8	23.4	8.8	8.6	73.6-73.7	243	18.9 18.9
<i>n</i> -Tetracosane - 1, 24 - diol (synthetic)	108.3-108.6	—	32.7	23.5	8.6	8.6	74.1-74.2	—	19.0 18.9
<i>n</i> -Hexacosane-1,26-diol ..	110.4-110.5	102-105‡	35.3	25.3	7.9	8.1	77.2-77.5	257	18.0 17.8
<i>n</i> -Octacosane-1,28-diol ..	112.2-112.3	—	37.7	26.8	7.5	7.6	80.9-81.0	258 (0.5 mm)	16.7 16.9
Undistilled diols ..	109.4-109.6	—	—	—	7.1	—	74.4-74.6	>264 (0.5 mm)	15.7 16.0 (C ₂₈)

* Shiina (1939).

† Soane, Gil Curbera, and Ribas (1953).

‡ Musgrave, Stark, and Spring (1952).

n-docosane-1,22-diol. The wide melting range reported by Musgrave, Stark, and Spring (1952) for *n*-hexacosane-1,26-diol suggests that their material was not pure. Mixed melting points were determined on the natural and synthetic diols and the corresponding diacetates, diacids, and dimethyl esters. In no case was a depression observed.

(iv) *Long Crystal Spacings*. Spacings were determined as published previously (Murray and Schoenfeld 1955). The four diols isolated and the synthetic diol showed two crystal forms designated *A* and *C* (a third form *B* giving intermediate spacings has been observed in later work). The values for the natural and the synthetic C_{24} diol again agree closely.

The identity of the C_{24} diol having been established, it follows from the values for the spacings that the four diols belong to a series of even carbon number. The longest spacings have differences of 2.5 Å which suggests that the *A* form is the perpendicular form, the interval of 2.5 Å corresponding to two carbons.

III. DISCUSSION

This work has shown that carnauba wax contains as constituents a series of even-numbered diols. Of these only the diols from C_{22} to C_{28} could be isolated by fractional distillation. However, a considerable amount of higher diols is also present, this being evident from the properties of the undistilled diol fraction. The proportion of these compounds may be as much as 40 per cent. of the total diols.

The total amount of diols present in the unsaponifiable fraction can be deduced from the final chromatogram. Fractions 3 to 5 constitute 5.9 per cent. of the total unsaponifiables, but if fraction 2 is also considered to be entirely diols, this value becomes 6.9 per cent. A good estimate of the proportion of diols among the alcohols of carnauba wax would thus be 6-7 per cent. An almost quantitative estimate of the distribution of the individual compounds within the diol mixture is obtained from the results of the amplified distillation. This is as follows: Below C_{22} (% calc. as C_{20}): 3; C_{22} 12; C_{24} 23; C_{26} 9; C_{28} 14; above C_{28} (undistilled) 39.

IV. ACKNOWLEDGMENTS

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STUDIES OF WAXES

XI. THE HYDROXY ACIDS OF CARNAUBA WAX

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Summary

Seven ω -hydroxy acids have been identified as constituents of carnauba wax. They are 18-hydroxyoctadecanoic, 20-hydroxyeicosanoic, 22-hydroxydocosanoic, 24-hydroxytetracosanoic, 26-hydroxyhexacosanoic, 28-hydroxyoctacosanoic, and 30-hydroxytriacontanoic acids.

I. INTRODUCTION

In an early investigation of the acids of carnauba wax Stürcke (1884) isolated a small acid fraction, m.p. 103.5°C , which he considered to be the lactone

of a hydroxy acid of the empirical formula $\text{C}_{19}\text{H}_{38}$ $\begin{matrix} \text{CH}_2\text{OH} \\ \diagup \\ \text{COOH} \end{matrix}$. No further

evidence for the presence of hydroxy acids was reported by later investigators until recently, when the present authors (Murray and Schoenfeld 1953) separated the normal and hydroxy acids by chromatography of their methyl esters on alumina. The present paper describes the investigation of the hydroxy acids separated in this way. A series of seven ω -hydroxy acids of even carbon number C_{18} to C_{30} has been shown to be present in carnauba wax. Separation was achieved by the amplified distillation of the acetylated methyl esters which were then identified by the reduction of each to the corresponding diol. The isolation of the free hydroxy acids for identification was avoided, in view of their likely contamination by estolides which readily form when salts of ω -hydroxy acids are acidified even under mild conditions (Jensen 1950a).

Hydroxy acids have frequently been reported as constituents of oils and occasionally of waxes from the earliest investigations until the present day. Some of these constituents were found on later investigation to be products of aerial oxidation, but a number proved to be major constituents of the unaltered oils and waxes. However ω -hydroxy acids have not been widely represented among the established hydroxylated components of fats and waxes. Saturated ω -hydroxy acids have been reported as constituents of various conifer waxes (Bougault and Bourdier 1909a, 1909b; Bougault 1910; Fujita and Yoshikawa 1951) and of angelica oil—in the latter case 15-hydroxypentadecanoic acid (Kerschbaum 1927). Jensen (1950b) has isolated 22-hydroxydocosanoic acid

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from the mixture of waxy acids obtained by the hydrolysis of suberin. Kamlo-lenic acid, the main unsaturated acid of kamala oil, has been shown to be 18-hydroxyeleostearic acid (Gupta, Sharma, and Aggarwal 1951; Calderwood and Gunstone 1953).

II. EXPERIMENTAL

Microanalyses were carried out in the C.S.I.R.O. Microanalytical Laboratory.

(a) *Saponification of the Wax*.—The unsaponifiable and acid fractions obtained on saponification of 250 g of carnauba wax ("Flores No. 1") were separated essentially as described previously (Murray and Schoenfeld 1953), with the exception that the acidic fraction extracted by ethyl acetate and previously referred to as "resin acids" was combined with the rest of the acids. This fraction from the previous work was found to be saponifiable and to have a low acid number (67). It was considered to consist of estolides formed from the hydroxy acids. The total acids represented 47.6% of the wax and the unsaponifiable 54.7%. The total recovery was 102.3% compared with a yield of 102.5% calculated from the saponification number of the wax. The acids had an acid number of 115 (acid equivalent 486 assuming only monobasic acids present) and an ester number of 35 (=sap. no.—acid no.). This appreciable ester number and the high acid equivalent suggested that a considerable fraction of the hydroxy acids had inter-esterified in the course of isolation and further work was based on this assumption.

(b) *Methylation of the Acids*.—(i) In order to obtain the methyl esters of the acids free from methylated estolides, a trial methylation under alkaline conditions was made on 5 g of the acids after first saponifying them with a slight excess of alcoholic KOH. The ethanol was then distilled off, the potassium soaps dispersed in benzene (200 ml), then dimethyl sulphate (4 ml) and anhydrous K_2CO_3 (10 g) added, and the whole refluxed for 1 hr. The recovered esters were chromatographed on alumina as described below for the main bulk of the esters. Three fractions were eluted by: (1) light petroleum (60–80 °C) (50% of the charge), (2) benzene-ethanol 1:1 (43%), and (3) chloroform-acetic acid 19:1 (6%). The acids recovered from fraction 1, which as shown in previous work should have been *n*-acids (Murray and Schoenfeld 1953), were found to contain 0.55% methoxyl. This fact taken with the larger bulk of this fraction than previously obtained indicated that a fraction (10–15%) of the terminal hydroxy groups of the hydroxy acids had also been methylated. It seemed likely that methylation by this method even under milder conditions would always involve some methylation of the terminal hydroxy groups and it was therefore abandoned.

(ii) The remainder of the acids were methylated by refluxing with methanol and benzene containing 1% sulphuric acid as previously described (Murray and Schoenfeld 1953). It had been observed in this laboratory that the lactones or lactides of wool wax could be methylated in this way to give the hydroxy acid methyl esters, and it was hoped that the estolides present in the carnauba acids would likewise undergo methanolysis to give complete methylation of the carboxyl groups (see Section III). The esters prepared in this way had an acid number of 3.

(c) *Separation of Normal and Hydroxy Esters*.—This separation followed the chromatographic procedure described previously (Murray and Schoenfeld 1953). The mixed acids (108.4 g) were divided into the following fractions:

Eluant	Vol. (ml)	Wt. (g)	%	M.p. (°C)
(1) Light petroleum (60–80 °C)	.. 2000	47.8	44.0	56–58
(2) Light petroleum (60–80 °C)	.. 1000	0.3	0.3	—
(3) Benzene-ethanol 1:1	.. 2500	41.6	38.4	73–74
(4) Chloroform-acetic acid 19:1	.. 3500	16.6	15.4	76–85

As found in our previous work, fraction 1 consisted almost entirely of normal esters. The proportion, however, was slightly higher than previously reported (38–39%). Fraction 3 (saponification number 136) contained most of the methyl hydroxy esters and was chosen for further study. Fraction 4 had a glassy resinous appearance and was brittle. It had an acid

number of 77, an ester number of 91, and a methoxyl content of 2.0%. The high acid number and the low methoxyl content indicated that appreciable demethylation had occurred during elution of this strongly adsorbed fraction. For this reason and because it was considered to contain methylated estolides (see Section III) it was not examined.

A portion (25.9 g) of fraction 3 was extracted with hot light petroleum (60–80 °C) which left some resinous substance (0.6 g) undissolved. The soluble material was acetylated with acetic anhydride at 100 °C for 6 hr, the excess anhydride being distilled off under vacuum, the last traces azeotropically with light petroleum (90–110 °C). The acetylated methyl esters were then chromatographed on neutral alumina at 40 °C to remove polar material. The light petroleum eluate weighed 21.7 g, had m.p. 68–71 °C and a saponification number of 228.

(d) *Separation of the Acetylated Methyl Esters by Amplified Distillation.*—Since it was intended to isolate the acetylated methyl esters after separation by amplified distillation (Weitkamp 1947) it was desirable to know their boiling points. These are represented by the distribution peaks when the saponification numbers of the fractions are plotted together with the distillation temperature. This information was obtained from a preliminary amplified distillation of 6 g of acetylated methyl esters obtained from a previous experiment, followed by saponification of the respective fractions. The results on plotting disclosed five distribution peaks corresponding to b.p. 206, 222, 238, and 252 °C (1.00 mm) and 251 °C (0.50 mm) respectively.

The above acetylated methyl esters (21.5 g) were then mixed with a selected mineral oil (107 g) and fractionally distilled in a 10 ft spinning band column (Murray 1951). Seventy-four fractions (c. 1.5 g) were collected between 154 and 260 °C at 1.00 mm and 244 and 266 °C at 0.5 mm pressure. On keeping these fractions at room temperature for several weeks the esters crystallized out and were separated after keeping at 0 °C for a further 18 hr. The fractions near the boiling points reported above contained a dense mass of crystals of the esters in the oil while intermediate fractions contained less crystalline material or none at all. Crystals were also observed in fractions close to 189 °C (at 1.00 mm) and 263 °C (at 0.50 mm). Fractions boiling within the range ± 3 °C of each of these seven temperatures were combined and the esters were isolated by filtering off the mineral oil, washing with cold light petroleum (50–60 °C), and crystallizing twice from the same solvent at 0 °C. The melting points are given in Table 1.

TABLE I
ACETYLATED METHYL ESTERS

Ester	Approx. Boiling Point (°C/1 mm)	Melting Point (°C)	Microanalyses						
			Found			Calculated			
			C	H	OCH ₃	Formula	C	H	OCH ₃
1	189	48.5–49.1	—	—	—	—	—	—	—
2	206	55.5–55.7	—	—	—	—	—	—	—
3	222	58.0–58.2	72.5	11.9	7.4	C ₂₅ H ₃₀ O ₄	72.5	12.1	7.5
4	238	63.2–63.4	73.3	12.1	6.9	C ₂₇ H ₃₄ O ₄	73.3	12.2	7.0
5	252	68.0–68.2	74.3	12.3	6.3	C ₂₉ H ₃₈ O ₄	74.0	12.3	6.6
6	251*	72.4–72.6	74.9	12.2	5.7	C ₃₁ H ₄₂ O ₄	74.7	12.4	6.2
7	263*	73.8–74.3	—	—	—	—	—	—	—

* At 0.5 mm pressure.

(e) *Reduction of the Esters to Diols.*—The seven acetylated esters isolated above were reduced with an excess of lithium aluminium hydride in ether. The crude diols were dissolved in benzene and chromatographed on alumina (Brockmann activity I/II) at 45 °C. More benzene was passed through the columns to remove possible traces of monoalcohols and the diols were then eluted with ethanol-benzene 1:1. They were twice recrystallized from the same solvent.

TABLE 2
DIOLS

Diol	Melting Point (°C)		Long Crystal Spacings (Å)			Microanalyses					
						Found			Calculated		
	Found	Literature	Present Work			C	H	O	C	H	O
			A Form	B Form	C Form						
1,18-Octadecane ..	98.1-98.4	98.6-99*	—	—	18.0	75.3	13.4	10.8	75.5	13.3	11.2
1,20-Eicosane ..	102.5-102.6	103*	—	—	19.8	76.6	13.3	10.3	76.4	13.4	10.2
1,22-Docosane ..	105.7-105.9	105.3-105.5† 105.6-105.7‡	30.2	—	21.6	76.9	13.6	9.6	77.2	13.4	9.3
1,24-Tetracosane ..	108.4-108.6	108.4-108.6‡	32.7	27.2	23.4	77.8	13.5	8.8	77.8	13.5	8.6
1,24-Tetracosane ..	—	108.3-108.6‡	32.7	27.1	23.5	—	—	8.6	—	—	8.6
1,26-Hexacosane ..	110.6-110.8	110.4-110.5‡	35.2	29.2	25.2	78.4	13.8	8.2	78.4	13.6	8.0
1,28-Octacosane ..	112.3-112.5	112.2-112.3‡	37.7	—	27.1	78.7	13.7	7.5	78.9	13.6	7.5
1,30-Triacotane ..	112.8-113.0	—	40.3	33.3	—	78.9	13.7	7.3	79.3	13.6	7.0

* Chitt and Hauser (1929).

† Shina (1939).

‡ Murray and Schoenfeld (1955).

|| Synthetic.

(f) *Identification of the Diols.*—The diols were characterized by their melting points, long crystal spacings, and microanalyses for carbon, hydrogen, and oxygen (Table 2).

Melting points were determined as previously described (Murray and Schoenfeld 1955a). There appeared to be phase change to an almost transparent form 1–2 °C below each melting point.

Long crystal spacings were also determined as in this previous work. The diffraction patterns gave spacing values which were assigned to three forms (*A*, *B*, and *C*) from their linear relation with chain length and by the different appearance of the patterns. The nature of the solvent appeared to have some influence on the form which predominated. When the C_{24} , C_{26} natural, and C_{24} synthetic diols (possibly the purest of the samples) were crystallized from ethanol-benzene 1:1 the *B* form predominated, but with less polar solvents such as acetone-benzene or toluene the *A* and *C* forms were favoured.

The crystalline appearance of the diols was examined microscopically using 2-ethyl hexanol as the solvent. They appeared in a flat regular rhombic form with acute profile angles of 58–60°. This form was indistinguishable from the usual form of other straight chain compounds (*n*-acids, *n*-alcohols, and *n*-paraffins).

The C_{24} diol was identified with synthetic 1:24 tetracosane diol (Murray and Schoenfeld 1955b) by agreement of m.p., mixed m.p., and long spacings. The C_{22} , C_{24} , C_{26} , and C_{28} diols were likewise identified with the four α - ω -diols previously isolated from the carnauba wax alcohols in the above work. Melting points of the C_{18} and C_{20} diols correspond with literature values for synthetic α - ω -diols. The homology of the series of the present diols is clearly established by their crystal spacings, melting points, microanalyses, and by the regularity of the boiling points of the esters from which they were derived.

(g) *Identification of the Hydroxy Acids.*—Four of the esters, those isolated in greatest amount, gave satisfactory microanalyses for carbon, hydrogen, and methoxyl for the acetylated methyl esters of C_{22} , C_{24} , C_{26} , and C_{28} hydroxy acids (Table 1). The C_{18} , C_{20} , and C_{30} esters gave only approximate analyses but after their reduction to diols insufficient ester remained for further purification. However, the identification of the seven polymethylene diols and the characterization of the four esters above provides ample evidence for the identification in the wax acids of a series of seven ω -hydroxy acids C_{18} to C_{30} .

III. DISCUSSION

In previous investigations of the *n*-alcohols, *n*-acids, and diols of carnauba wax (Murray and Schoenfeld 1951, 1953, 1955b) it was possible to give a nearly quantitative estimation of the proportions of the members of each homologous series. The present work is only qualitative because during the isolation of the free hydroxy acids some estolides were formed. These estolides were not entirely converted to the hydroxy acid methyl esters by methanol and sulphuric acid. They were separable by chromatography and appeared in the chloroform-acetic acid eluate (fraction 4). That this fraction contained esters other than methyl follows from the difference between its methoxyl content (2.0 per cent.) and that calculated from its ester number (5.5 per cent.). Furthermore when methylation of the total acids was performed under alkaline conditions the corresponding fraction of the resulting methyl esters was much smaller. Investigation of fraction 4 was not attempted but it was included when forming an estimate of the ω -hydroxy acids and on this basis they constitute approximately 60 per cent. of the carnauba wax acids. The hydroxy acids appear to be in the following order of abundance: $C_{24} > C_{26}$, $C_{28} > C_{22}$, $C_{30} > C_{20} > C_{18}$, as indicated by the relative yields of the corresponding acetylated methyl esters. This same order was observed in the preliminary amplified distillation.

This work concludes an investigation of the constituent acids and alcohols of carnauba wax, which was undertaken to develop and apply fractional distillation methods, particularly amplified distillation to the investigation of waxes generally. Although carnauba wax was chosen as a relatively simple wax 23 constituent compounds have been identified. It is doubtful whether it would have been possible by any other existing method to isolate and fully characterize so many components some of which could be regarded only as minor components.

As a result of our work it is now possible to state the composition of hydrolysed carnauba wax:

Carnauba Wax ("Flores No. 1"):

(i) *Unsaponifiable fraction (55-57% of the wax):*

Hydrocarbons (less than 1%), a complex mixture.

n-Alcohols (93-94%), C₂₄, C₂₈, C₃₀, C₃₂, C₃₄.

α - ω -Diols (6-7%), C₂₂, C₂₄, C₂₆, C₂₈, and higher.

(ii) *Acids (45-47% of the wax):*

n-Acids (c. 40%), C₁₈, C₂₀, C₂₂, C₂₄, C₂₆, C₂₈, C₃₀.

ω -Hydroxy acids (c. 60%), C₁₈, C₂₀, C₂₂, C₂₄, C₂₆, C₂₈, C₃₀.*

Compositions of unhydrolysed carnauba wax have been published by Warth (1947) and by Findlay and Brown (1953). The hypothetical nature of Warth's composition and the lack of evidence for the esters he enumerates have already been commented on by Findlay and Brown. These latter workers attempted to ascertain the composition from methods of functional group analysis applied to the unhydrolysed wax and to the unsaponifiable fraction. Their calculations could be of considerable value, but in order to be so, the determinations employed must be of high accuracy or the results can be most misleading. In particular the Rast determination of molecular weight which they use is well known to provide only a very approximate value. Findlay and Brown's value for the hydrocarbon content of carnauba wax is an example of the misleading conclusions which may result. Stürcke (1884) had already reported the presence of small amounts of hydrocarbons. This we confirmed (Murray and Schoenfeld 1951) and the amount was found to be less than 1 per cent. Nevertheless Findlay and Brown report a value of 11 per cent. This value they obtained assuming that only monohydric alcohols were present, although Stürcke and Murray and Schoenfeld (1951) had previously reported the presence of diols. If Findlay and Brown had used the diol content of 6-7 per cent. now reported then the reputed hydrocarbon content would have been still greater.

The examination by Findlay and Brown (1953) of several other hard vegetable waxes (caranda, candelilla, curicury) has however indicated without doubt the presence in all of them of considerable amounts of hydroxy acids, so that it is possible that the occurrence of the ω -acids in waxes is widespread. The procedure outlined in the present paper could also be used for their detailed quantitative examination provided they could be methylated without polyester formation or without the methylation of the terminal hydroxy group on which their separation from the normal esters depends. Failing this the hydroxy

acids could be separated from the *n*-acids as described here, followed by their complete methylation under alkaline conditions. The ω -methoxy acids would then be isolated after distillation and saponification of the fractions and identified as such.

The presence in carnauba wax of esters of ω -hydroxy acids may well explain its outstanding and desirable physical properties. It is well known that the addition of a small proportion of carnauba wax to other lower melting waxes gives products of greatly increased melting points, and it forms gels with solvents of high strength. Perhaps this is due to the formation of even small amounts of polyestolides or polyesters of long chain length from these hydroxy acids which would have a pronounced effect on the physical properties of the wax. It may be that the resins mentioned by Warth (1947) and apparently unexamined are such polyester compounds.

IV. ACKNOWLEDGMENT

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WATER-SOLUBLE CONSTITUENTS OF FRUIT

V. SUGARS AND POLYOLS OF THE APRICOT FRUIT*

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Summary

The sugars and polyols of the apricot fruit were separated by chromatography on columns of charcoal and cellulose followed, where necessary, by paper chromatography. Glucose and sorbitol were separated by chemical methods. Xylose, fructose, glucose, sucrose, sorbitol, and mesoinositol were characterized, xylose as the dibenzylidene dimethylacetal, fructose as the 2,5-dichlorophenylhydrazone, glucose as the diethyl-mercaptal, sucrose as the octa-acetate, and sorbitol and mesoinositol as the hexa-acetates. A number of apricot oligosaccharides composed of glucose and fructose units were separated by chromatography on charcoal and on paper.

I. INTRODUCTION

Glucose, fructose, and sucrose are generally considered to be the major sugars in edible fruits. There are some early reports (1806–1909; see von Lippmann 1904, Beilstein 1938) of the isolation of one or other of these sugars from fruit but there have been few attempts to confirm this work by modern methods. The apricot fruit has been studied by several workers. Buignet (1861) isolated sucrose from it and Proust (1806) obtained a few crystals which may have been glucose. Vincent and Delachanal (1889) isolated sorbitol as the hexa-acetate and this was confirmed by Reif (1934) who isolated the benzal derivative.

The sugars and polyols of the apricot fruit have now been examined by chromatographic methods; the results obtained from paper chromatograms have already been described (Ash and Reynolds 1955). In extending the work to column chromatography the separation was made in two or more stages. A charcoal column (Whistler and Durso 1951), pretreated with stearic acid to block the most active adsorption centres (cf. Alm 1952), was used for the first stage. This fractionation produced three groups which could be broadly described as monosaccharides, sucrose, and oligosaccharides; the fractions which contained the bulk of the sucrose yielded the crystalline sugar directly.

The monosaccharide fractions (which also contained the polyols and some sucrose) were chromatographed on cellulose columns run at an elevated temperature (cf. Counsell, Hough, and Wadman 1951). A typical fractionation is shown in Table 1. Inositol was obtained by evaporating the later fractions;

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the monosaccharides and sorbitol were finally separated by chemical methods or by paper chromatography.

TABLE 1
FRACTIONATION OF MONOSACCHARIDES, POLYOLS, AND SUCROSE
ON A CELLULOSE COLUMN AT APPROXIMATELY 64 °C* (DEVELOPED
WITH *n*-BUTANOL-WATER 94:15)

Fraction No.†	Group	Sugars and Polyols detected by Paper Chromatography
0-34	—	Nil
35-45	A	Xylose, and traces of fructose
46-49	B	Xylose and fructose
50-61	B	Fructose and traces of glucose and sorbitol
62-81	C	Glucose and sorbitol
82-92	—	Traces of glucose and sorbitol
93-146	D	Sucrose
147-149	—	Nil
150-221	E	Inositol

* The column was enclosed in a glass jacket in which methanol was refluxed.

† Volume approx. 11 ml.

The oligosaccharide fractions from the first charcoal column were chromatographed again on charcoal using a much smaller column. The results of the

TABLE 2
FRACTIONATION OF OLIGOSACCHARIDES ON A CHARCOAL COLUMN (DEVELOPED
WITH ETHANOL-WATER)

Fraction No.*	Developing Solvent % Ethanol in Water	Sugars detected by Paper Chromatography†
1-2	1	Nil
3-4	1	Sucrose
5-6	1-2	Nil
7-9	2	Sucrose, K1, A1, and traces of other sugars
10-11	2	A1, K2, and K3
12	2	K3 and traces of other sugars
13-53	2	K3
54-62	2-2.5	Traces of K3, K4, and K5
63-69	2.5	K4, K5, and K6
70-82	3	K4
83-95	4	K4 tailing

* Volume approx. 45 ml.

† K1-K6 gave a ketose reaction; A1 reacted as an aldose.

fractionation are shown in Table 2. The oligosaccharide K3 was chromatographically pure but could not be crystallized. The other oligosaccharides

were eventually separated by paper chromatography with the exception of A1 which could not be separated completely from K3.

The present work has resulted in the separation of virtually all the sugars and polyols in the apricot fruit. Sucrose, glucose, fructose, xylose, sorbitol, and mesoinositol have been characterized by the preparation of suitable crystalline derivatives. Sorbitol appeared to be the only hexitol present. An apparently new oligosaccharide (K3) has been separated but not crystallized; it has been suggested that this compound is a trisaccharide of the type *O*- α -D-glucopyranosyl-(1 \rightarrow 2)-*O*- β -D-fructofuranosyl-(?)- β -D-fructofuranoside (Ash and Reynolds 1954b). The remaining carbohydrates in the extracts were oligosaccharides which were present in minute amounts (each less than 0.003 per cent. of the fresh fruit). One of these probably contained only glucose, one contained fructose and a hexitol, and the others glucose and fructose.

II. EXPERIMENTAL

Melting points are uncorrected. Solutions were evaporated under reduced pressure (bath temp. $\geq 4^{\circ}\text{C}$) using rotary evaporators. Microanalyses were carried out in the C.S.I.R.O. Microanalytical Laboratory.

(a) *Preparation of Extract.*—An aqueous solution was prepared from an 80% alcoholic extract of ripe apricot fruit (variety Trevatt) and de-ionized by passing through columns of "Zeo Carb 225" and "Amberlite IR-4B" ion-exchange resins (Anet and Reynolds 1955, Section IV (c)). This solution was concentrated to c. 10% total sugar content.

(b) *Preparation of Charcoal Columns.*—A mixture of equal weights of "Norit CF" charcoal and "Dicalite No. 4200" filter-aid was allowed to stand in contact with a solution of stearic acid (1% in 95% ethanol) for 48 hr with occasional stirring. The mixture was slurried into a chromatography column and excess stearic acid was removed by washing with 95% ethanol until the effluent remained clear on dilution with water. The ethanol was displaced with deaerated 50% ethanol and then with water. In later work "Norit CF" charcoal was shaken, or stirred continually, with a solution of stearic acid (0.5% in 95% ethanol) for 4 hr and washed on a filter with 95% ethanol until free from excess stearic acid. The charcoal was then washed with water, dried, and mixed with an equal weight of "Dicalite No. 4200". Charcoal more heavily blocked with stearic acid had a lower capacity for sugars and the separation was not improved.

(c) *Preparation of Cellulose Columns.*—The method was devised to overcome the difficulty experienced in preparing a column free from air bubbles. Cellulose powder (Whatman Standard Ashless) which passed through 100 mesh was used. A chromatography column (30 \times 550 mm) was enclosed by a glass jacket in which methanol was refluxed whilst the column was packed as a slurry in the solvent subsequently used for development (*n*-butanol-water, 94 : 15). Both the solvent and the slurry were deaerated at 60–70 $^{\circ}\text{C}$. The tapered part of the column was filled with acid-washed sand (run in as a slurry in the developing solvent) on top of a glass-wool plug. The cellulose slurry was added in small portions and each portion (about 1 in. depth) was pressed down firmly with a stainless-steel tamper. Heavy metals were then removed from the cellulose with 8-hydroxyquinoline (45 ml 2% solution in butanol-water, applied as three bands and washed through with butanol-water). Between runs the column was stored at 50 $^{\circ}\text{C}$.

(d) *Separation of Sucrose from Polyols and Mono- and Oligosaccharides on a Charcoal Column.*—The column (60 mm diameter) used contained 500 g of charcoal-"Dicalite" mixture prepared by the first method described above. The column was run under slight suction. Concentrated de-ionized extract (equiv. to 440 g fresh fruit; c. 40 g total sugar containing c. 30 g sucrose) was run onto the column and the chromatogram was developed by the successive application of water (36 l.), 2.5% ethanol (10 l.), 5% ethanol (5 l.), and 15% ethanol (5 l.). Fractions of 1 and 2 l. were collected and tested for sugars with α -naphthol-sulphuric acid (Brown and Serro 1953) or resorcinol-hydrochloric acid (Seliwanoff test for ketoses, Beilstein 1918). Aliquots of selected fractions were concentrated and examined by paper chromatography using the solvents and

reagents previously described (Ash and Reynolds 1954a and 1955). The monosaccharides and polyols and some sucrose were eluted in the first 2 l. of water and the bulk of the sucrose in the following 34 l. of water and 10 l. of 2.5% ethanol. The higher concentrations of ethanol eluted and partially separated the oligosaccharides but all fractions contained a little sucrose.

(c) *Separation of Polyols and Monosaccharides on a Cellulose Column.*—The monosaccharide fraction (containing also polyols and sucrose) from the charcoal column was evaporated to dryness. An aliquot (2.7–3.0 g) of the residue was taken up in a little water and applied as a thin syrup to the top of the cellulose column (with methanol refluxing in the jacket). The chromatogram was developed with *n*-butanol-water (94:15); the flow rate was 0.4–0.6 ml/min and fractions (each approx. 11 ml) were collected automatically at 20 min intervals. Fractions which gave a positive reaction with an α -naphthol reagent (Brown and Serro 1953) were examined by paper chromatography; usually 6 μ l of each fraction were applied to the papers but 20 μ l were used to detect the extremities of the bands. The concentrations in which the compounds were eluted from the column decreased with R_F value. The separation achieved is shown in Table 1. For further work the fractions were bulked into five groups (A–E; Table 1). Similar results were obtained in two further runs and corresponding groups of fractions from the three runs were combined.

(f) *Characterization of Sugars and Polyols.*—(i) *Sucrose.* An aliquot of the sucrose fraction from the charcoal column was evaporated and the resultant syrup crystallized by dissolving in warm water and adding ethanol. After recrystallization from aqueous ethanol the m.p. was 183–184 °C not depressed by an authentic sample; $[\alpha]_D^{20} + 66.0^\circ$ (c, 10 in water). The sugar was acetylated with acetic anhydride using sodium acetate as catalyst. The octa-acetate was recrystallized from 95% ethanol, m.p. 84–85 °C not depressed by an authentic sample (Found: C, 49.5; H, 5.8; O, 44.6%. Calc. for $C_{28}H_{38}O_{19}$: C, 49.5; H, 5.7; O, 44.8%).

(ii) *D-Xylose.* Solution B from the cellulose columns (containing xylose and fructose with traces of glucose and sorbitol) was concentrated and applied as streaks to Whatman No. 3 MM filter paper. Haemocytometer pipettes were used and the total sugar load on a 24 by 24 in. sheet was 80 mg. The chromatograms were run in ethyl acetate-pyridine-water (8:2:1) and xylose was eluted from appropriate strips. These eluates were combined with solution A from the cellulose columns and evaporated to dryness (90 mg. containing some fructose from solution A). The dibenzylidene dimethylacetal (Breddy and Jones 1945) after recrystallization from chloroform-light petroleum, had m.p. 209–210 °C not depressed by an authentic specimen (Found: C, 67.6; H, 6.7; O, 25.4%. Calc. for $C_{21}H_{24}O_6$: C, 67.7; H, 6.5; O, 25.8%).

(iii) *D-Fructose.* The fructose in solution B from the cellulose columns was recovered by elution from the paper chromatograms described above. It was separated from traces of xylose and glucose by chromatographing it again on Whatman No. 3 MM paper in the same solvent. The optical rotation of the eluted fructose (0.15 g), $[\alpha]_D^{20} -92.1 \pm 0.4^\circ$ (c, 2.42 in water), was determined after correcting for the weight of contaminant material (10 mg, optical rotation nil) eluted from an equivalent number of paper strips. The 2,5-dichlorophenylhydrazone was prepared (Mandl and Neuberg 1952) and recrystallized three times from dry dioxane. It was difficult to crystallize from other solvents. After drying for 48 hr *in vacuo* at room temperature over phosphorus pentoxide and paraffin wax the m.p. was 152 °C, not depressed by an authentic specimen. The hydrazone appeared to contain one molecule of dioxane (Found: C, 45.2; H, 5.6; O, 25.4; Cl, 17.0%. Calc. for $C_{12}H_{16}O_2N_2Cl_2C_4H_8O_2$: C, 44.9; H, 5.7; O, 26.2; Cl, 16.6%). An authentic specimen was analysed before and after drying *in vacuo* at 80 °C for 3 hr; the dioxane was apparently not removed by this treatment (Found, before drying: C, 45.1; H, 5.9; O, 25.7%. Found, after drying at 80 °C: C, 45.2; H, 5.8; O, 25.5%). Mandl and Neuberg (1952) state that analyses confirmed the theoretically calculated composition of a series of 2,5-dichlorophenylhydrazones, but it is not clear whether or not the fructose derivative was recrystallized from dioxane before analysis.

(iv) *D-Glucose and D-Sorbitol.* Solution C from the cellulose columns was evaporated to dryness and the residue (2.5 g) treated with fuming hydrochloric acid (2 ml) and ethyl mercaptan (2 ml) (Zinner 1951). The crude mercaptal was recrystallized once from water and three times

from methanol giving colourless needles, $[\alpha]_D^{20} -8.9^\circ$ (c, 1.34 in methanol), m.p. 128°C not depressed by authentic D-glucose diethylmercaptal (Found: C, 41.8; H, 7.8; O, 27.8; S, 22.4%. Calc. for $\text{C}_{16}\text{H}_{24}\text{O}_8\text{S}_2$: C, 41.9; H, 7.7; O, 28.0; S, 22.4%). The filtrate from the mercaptal preparation was passed through a column of anion-exchange resin ("Amberlite IR-4B") to remove the hydrochloric acid. The eluate was evaporated to a syrup which was then dried and dissolved in hot pyridine (5 ml). Crystals separated on standing in a vacuum desiccator over sulphuric acid. The m.p., $71-74^\circ\text{C}$, was unchanged on admixture with the pyridine complex of authentic sorbitol dried under the same conditions.* The complex was decomposed with water and evaporated to dryness. A small sample of the resultant gum was taken up in 95% ethanol and the solution allowed to evaporate at room temperature. A white solid was left which had m.p. $89-93^\circ\text{C}$, alone or on admixture with authentic anhydrous D-sorbitol. The remainder of the gum was acetylated with acetic anhydride in the presence of pyridine (Tutin 1925). After three recrystallizations from 95% ethanol the acetylated compound had m.p. $99-100^\circ\text{C}$, not depressed by authentic D-sorbitol hexa-acetate (Found: C, 49.7; H, 6.3; O, 44.0%. Calc. for $\text{C}_{18}\text{H}_{26}\text{O}_{12}$: C, 49.8; H, 6.0; O, 44.2%).

The filtrate from the preparation of the pyridine-sorbitol complex was evaporated and the residue chromatographed on Whatman No. 3 MM paper. Unreacted hexitol was eluted (yield 20 mg) and acetylated. The acetyl compound, after one recrystallization, had m.p. 98°C alone and 99°C on admixture with authentic D-sorbitol hexa-acetate.

(v) *mesoInositol*. Solution E from the cellulose column was evaporated to dryness (0.14 g). The residue gave a positive colour reaction for inositol (Scherer 1852) and a sample was crystallized from 95% ethanol. The m.p. was $122-123^\circ\text{C}$ not depressed by authentic *meso*inositol. The remaining syrup was acetylated with acetic anhydride using zinc chloride as catalyst (Müller 1907). The acetylated compound was decolorized with animal charcoal and recrystallized from 95% ethanol and from benzene-light petroleum. The m.p. was $214-215^\circ\text{C}$, not depressed by authentic *meso*inositol hexa-acetate (Found: C, 50.0; H, 5.7; O, 43.9%. Calc. for $\text{C}_{18}\text{H}_{26}\text{O}_{12}$: C, 50.0; H, 5.6; O, 44.4%).

(g) *Separation of Oligosaccharides*.—(i) *Fractionation on a Charcoal Column*. The 5 and 15% ethanol eluates from the charcoal column (Section II (d)) were combined and evaporated to dryness. A 10% aqueous solution of the resultant gum (0.7 g) was applied to the top of a column (19 mm diameter) which contained 23 g of charcoal-"Dicalite" mixture prepared by the later method (Section II (b)). Using a flow rate of 0.5 ml/min (maintained by using a slightly raised reservoir) the column was washed with water (250 ml) and the oligosaccharides were eluted with 1, 2, 2.5, 3, and 4% ethanol and fractions (approx. 45 ml) collected. The separation of the oligosaccharides is shown in Table 2. Those which gave a ketose reaction on paper chromatograms sprayed with naphthoresorcinol-trichloroacetic acid were designated K1-K6 and numbered in order of emergence from the charcoal column. Oligosaccharide A1 did not give a ketose reaction.

(ii) *Separation on Paper*. Fractions 7-11 from the smaller charcoal column (Table 2) were combined, concentrated, and run twice on Whatman No. 3 MM paper in ethyl acetate-pyridine-water (8:2:1) (cf. Section II (f) (ii)). This separated oligosaccharides K1 and K2, but A1 could not be completely separated from K3. In later work K1 was resolved into two components by a long run (64 hr on Whatman No. 4 paper) in *n*-butanol-acetic acid-water (4:1:1).

Fractions 54-82 (Table 2) were concentrated and chromatographed once as described above. This separated oligosaccharides K4, K5, and K6.

(h) *Examination of Oligosaccharides*.—(i) *Oligosaccharide K3*. Fractions 13-53 (Table 2) were evaporated to dryness (0.3 g). The residue appeared to be chromatographically pure when run in several solvents but it could not be crystallized. The rotation was $[\alpha]_D^{20} +24.3^\circ$ (c, 4.94

* The authentic complex, for which Strain (1934) records a m.p. of 89°C , had the same m.p. ($71-74^\circ\text{C}$) after several recrystallizations from pyridine and after drying for 3 weeks over phosphorus pentoxide. The lower m.p. may be due to strongly adsorbed pyridine (cf. Strain 1934).

in water). K3 was completely hydrolysed by yeast invertase (4 hr at 32 °C) to glucose and fructose which were separated on paper chromatograms (No. 1 Whatman) run for 64 hr with ethyl acetate-acetic acid-water (3 : 1 : 3; Jermyn and Isherwood 1949), this solvent giving the most satisfactory separation for quantitative determination. The sugars were eluted and determined by the anthrone (Fairbairn 1953) reaction; the ratio glucose : fructose was 1 : 2. The syrup obtained by the hydrolysis of K3 with 20% acetic acid at 50 °C for 4 hr was examined by paper chromatography using the solvents and reagents previously described (Ash and Reynolds 1954a, 1955); samples of authentic sugars were run on the same chromatograms. The hydrolysate contained three sugars which appeared to be glucose, fructose, and sucrose. Some of the sugar presumed to be sucrose was eluted and treated on paper (Williams and Bevenue 1951) with invertase which hydrolysed it completely to glucose and fructose. K3 was a non-reducing sugar (3,5-dinitrosalicylic acid reagent; Jeanes, Wise, and Dimler 1951).

(ii) *Other Oligosaccharides.* The oligosaccharides K2, K4, K5, and K6 (each c. 10 mg or less) were non-reducing and gave only glucose and fructose when hydrolysed on paper with yeast invertase; although the papers were incubated at 32 °C a little unchanged oligosaccharide was usually detected. *R_S* values of the ketose oligosaccharides have been recorded (Ash and Reynolds 1954b).

The oligosaccharide designated K1 in Table 2 was hydrolysed with invertase and gave glucose, fructose, and a hexitol which behaved like sorbitol on paper chromatograms. When K1 was resolved (Section II (g) (ii)) into two components (*R_S*, 0.72 and 0.86) it was found that both gave a ketose reaction and the component with the lower *R_S* value was a reducing sugar.

The oligosaccharide A1 was virtually freed from contamination with K3 by treatment with formic acid (43% at 100 °C for 30 min) which hydrolysed K3 to glucose and fructose but left A1 apparently unchanged. A1 gave strong spots with aniline phosphate and silver nitrate-sodium hydroxide but did not react with naphthoresorcinol-trichloroacetic acid. A1 was partially hydrolysed with 85% formic acid giving glucose.

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SHORT COMMUNICATIONS

THE MOLECULAR COMPLEXITY OF POLAR ORGANIC VAPOURS*

By L. A. BENNETT† and R. G. VINES†

Gas imperfection may always be treated theoretically as a case of molecular association (Beattie and Stockmayer 1951; Francis 1953; Lambert 1953). The concept is rarely adopted in practice, except with polar vapours such as acetic or formic acids, or when direct spectroscopic evidence of association is available, cf. also the studies of fluorescence in acetone vapour (Kaskan and Duncan 1950). In an investigation of the variation with pressure of the thermal conductivities of organic vapours (Vines 1953), the idea was used to explain the behaviour of strongly polar compounds. However, it was pointed out that no sharp distinction could be made between molecular association and extensive dipole interaction; that is, it was not possible to distinguish between polar compounds which form associated dimers capable of surviving a large number of molecular collisions, and those where strong interaction leads merely to transient dipole complexes which are dispersed after very few impacts. This would require information regarding the lifetime of the association complex. However, additional measurements now suggest that these two types of molecular interaction may be clearly differentiated by thermal conductivity methods.

The treatment of Lambert *et al.* (1949) implies that, in a polar vapour, gas imperfection may be considered to consist of two parts. The first is due to van der Waals forces, and is adequately represented by the Berthelot equation: the second is due to molecular association. Both contribute to the variation of the thermal conductivity with pressure. Thus, if β is the percentage increase in conductivity over a pressure range of 1 atm, the experimentally observed value of β is given by

$$\beta_{\text{obs.}} = \beta_{(d)} + \beta_{\text{Berthelot}} \dots \dots \dots (1)$$

Here $\beta_{(d)}$ is the β -value attributable to association (dimerization), and $\beta_{\text{Berthelot}}$ may be evaluated in terms of critical constants (see Vines 1953).

It was shown previously that

$$\beta_{(d)} = 100(\Delta U^2)/RT^2K_pC_{v_0} \dots \dots \dots (2)$$

where ΔU is the heat of association at constant volume, R the gas constant, K_p the equilibrium constant of the dissociation process, T the temperature, and C_{v_0} the molar heat capacity of the vapour. In the derivation of this expression it is assumed that association produces only a thermal effect which contributes to the conduction process. If, however, the association complex has a

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considerable lifetime, allowance must be made for the fact that the mean free paths and collision diameters of associated molecules are different from those of single molecules. The work of Schäfer and Foz Gazulla (1942) suggests that this will decrease the value of $\beta_{(d)}$, and that equation (2) should be replaced by

$$\beta_{(d)} \approx 41 \cdot 2 (\Delta U^2) / RT^2 K_p C_{v_0} \quad \dots \dots \dots (3)$$

Equations (2) and (3) are identical but for the proportionality constants, which differ by a factor of $\sim 2 \cdot 5$. Thus, if experimental values of $\beta_{(d)}$ for a polar vapour are in good agreement with values calculated from equation (2), it may be inferred that molecular interaction is confined to strong dipole attraction. On the other hand, if the values so calculated are roughly 2.5 times the experimental values (i.e. if eqn. (3) is more appropriate than eqn. (2)), then definite association of the molecules is indicated. The behaviour of a number of polar vapours in this respect is discussed in this paper.

TABLE 1
HEATS OF ASSOCIATION CALCULATED FROM THE VARIATION OF $\beta_{(d)}$ WITH TEMPERATURE

Vapour	$\beta_{(d)}$ *	Mean T (°C)	C_{v_0} (cal mole ⁻¹)	ΔH (calc.) (cal mole ⁻¹)	ΔH (expt.) (cal mole ⁻¹)
Nitromethane ..	4.86 at 110 °C 2.36 at 149 °C	130	14.8 ^(a)	3900	4000 ^(d)
Acetonitrile ..	7.30 at 109 °C 4.82 at 126 °C	117	12.5 ^(b)	5300	5200 ^(c)
Water vapour ..	1.91 at 126 °C 1.15 at 149 °C	138	6.22 ^(c)	5700	5200 ^(f)

* Experimental values of $\beta_{(d)}$, as listed in Table 2.

^(a) De Vries and Collins (1942). ^(b) Thompson (1941). ^(c) McCullough, Pennington, and Waddington (1952). ^(d) From the vapour density measurements of Pitzer and Gwinn (1941): Following the method of Lambert *et al.* (1949), a Clausius-Clapeyron plot was obtained from the values of the second virial coefficient at various temperatures. The slope of the resultant straight line gave $\Delta H \approx 4000$ cal mole⁻¹. ^(e) From compressibility measurements of Lambert *et al.* (1949). ^(f) From calculations of Rowlinson (1949).

Differentiation of either equation (2) or (3) leads to the expression

$$\frac{d[\log \beta_{(d)}]}{d(1/T)} = \frac{\Delta H}{R} + 2T + \frac{T^2}{C_{v_0}} \cdot \frac{dC_{v_0}}{dT}, \quad \dots \dots \dots (4)$$

from which ΔH , the heat of association at constant pressure, may be calculated from the temperature variation of $\beta_{(d)}$ (see Vines 1953).

From equation (4) values of ΔH have been obtained for nitromethane, acetonitrile, and water vapour, using the recent experimental measurements of Vines and Bennett (1954). The results agree well with values obtained by other methods, and are shown in Table 1.

Since $\Delta H = \Delta U + RT$ values of ΔU may be obtained from Table 1. If these are now substituted in equation (2), $\beta_{(d)}$ may be calculated. The results are shown in Table 2.

For acetonitrile and water vapour the values obtained are about 2.5 times greater than experimental values; this is in agreement with previous observations for methanol, acetone, and acetaldehyde (Vines 1953). The inference is that all these molecules associate, and that corrections are necessary for the changed mean free paths and collision diameters of the dimers, cf. equation (3).

TABLE 2
COMPARISON OF EXPERIMENTAL VALUES OF $\beta_{(d)}$, WITH VALUES CALCULATED* ON THE ASSUMPTION OF MOLECULAR ASSOCIATION

Vapour	T (°C)	$\beta_{\text{obs.}}^\dagger$	$\beta_{\text{Berthelot}}$	$\beta_{(d)}$ ($=\beta_{\text{obs.}} - \beta_{\text{Berthelot}}$)	$\beta_{(d)}$ calc. 2.5	$\beta_{(d)}$ calc.
Nitromethane	110	5.55	0.69	4.86	—	4.82 ^(a)
	149	2.85	0.49	2.36	—	2.33
Acetonitrile . .	109	8.15	0.85	7.30	7.05 ^(b)	—
	126	5.55	0.73	4.82	4.68	—
	149	3.0	0.59	2.41	2.81	—
Water vapour	101	3.25	0.66	2.59	2.74 ^(c)	—
	109	2.95	0.62	2.33	2.23	—
	126	2.45	0.54	1.91	1.48	—
	149	1.60	0.45	1.15	0.90	—

* Values used in calculations:

^(a) $\Delta U = 3,100$ (Table 1); $C_{v0} = 14.36$ at 110 °C, 15.24 at 149 °C (De Vries and Collins 1942); $K_p = 47.3$ and 75.85 respectively (from Pitzer and Gwinn (1941), see footnote to Table 1).

^(b) $\Delta U = 4,500$ (Table 1); $C_{v0} = 12.3$ at 109 °C, 12.7 at 126 °C, and 13.2 at 149 °C (Thompson 1941); $K_p = 31.8$, 42.75, and 61.4 respectively (Rowlinson 1949).

^(c) $\Delta U = 4,900$ (Table 1); $C_{v0} = 6.14$ at 101 °C, 6.16 at 109 °C, 6.19 at 126 °C, and 6.24 at 149 °C (McCullough, Pennington, and Waddington 1952); $K_p = 203.2$, 238.8, 329.6, and 487.5 respectively (Rowlinson 1949).

[†] Experimental values of Vines and Bennett (1954) and Vines (1953): $\beta_{\text{Berthelot}}$ is calculated from critical constants.

However, the correction factor of 2.5 is not necessary for nitromethane. This suggests the absence of collision complexes of long lifetime, which is not surprising as hydrogen bonding in the vapour state is unlikely with nitromethane. On the other hand, since strong hydrogen bonding occurs with substances such as methanol and water vapour, associated molecules of long life are to be expected.

Nevertheless association does not appear to be entirely dependent upon hydrogen bond formation; otherwise the behaviour of acetonitrile is difficult to understand (though here hydrogen bonding might possibly occur in the imino-form). Further work is undoubtedly necessary, but it is clear that the study of molecular interaction by thermal conductivity methods may have considerable value.

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THE INFLUENCE OF $-I+M$ GROUPS IN AROMATIC S_N REACTIONS*

By R. L. HEPPOLETTE,† M. LIVERIS,† P. G. LUTZ,‡ J. MILLER,†
and V. A. WILLIAMS§

With the measurement of rate constants and Arrhenius parameters for the replacement of Cl in (i) 2-chloro-3,5-dinitroanisole and in (ii) 1,4-dichloro-2,6-dinitrobenzene by OMe^- in absolute MeOH (Table 1), it is now convenient to bring together and compare the substituent effects at all positions of representative members of that class of substituent attached to the benzene ring by a hetero-atom in the electrically neutral condition.

TABLE I
MEASUREMENT OF RATE CONSTANTS FOR THE REPLACEMENT OF Cl

Compound	Rate Constants 10^3k_2 ($1 \text{ mol}^{-1} \text{ sec}^{-1}$) for Temperatures ($^{\circ}\text{C}$)								Activa- tion Energy (cal)	Log_{10} Fre- quency Factor
	Given in Parentheses					Calculated at :				
						0	50	100		
2- Chloro - 3 , 5 - dinitroanisole	1.16 _a (15.0)	2.05 (20.0)	2.57 (25.0)	6.45 (30.2)	29.0 (45.3)	0.181	46.7	2610	19400	11.8
1, 4 - Dichloro - 2, 6 - dinitroanisole	2.01 (14.0)	3.53 (19.65)	9.56 (29.4)	16.4 (35.45)		0.423	58.6	2160	17300	10.4 ₂

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Substituent effects have been discussed by one of us (Miller 1951) for aromatic S_N reactions and certain predictions made. Table 2 lists the substituent rate factors (S.R.F., Miller 1952) for Cl, OMe, and NH_2 at *ortho*-, *meta*-, and *para*-positions, and compares them with the predictions.

The groups chosen come from Groups V, VI, and VII of the Periodic Table, and are all classified for aromatic S_N reactions, as $-I+M$ (Miller 1951), though in different subgroups.

Chlorine as a typical halogen has a greater $-I$ than $+M$ effect. The former activates in the order $o>m>p$, while the latter deactivates in the order $m>o>p$, however the relative operation of the effects should be to give the order $m>o>p$

TABLE 2
SUBSTITUENT RATE FACTORS

Substituent	Temp. (°C)	Substituent Rate Factors			Predicted Effect
		<i>Ortho</i>	<i>Meta</i>	<i>Para</i>	
Cl*	0	21.5	—	18.8	$o>m>p$; all similar, and all weakly activating
	50	12.0	—	14.0	
	100	7.84	—	11.2	
Cl†	0	3.72	7.20	8.49	$o>m>p$; all similar, and all weakly activating
	50	(11.4)‡	(4.00)	7.91	
	100	(25.9)	(2.59)	7.50	
OMe†	0	0.0906	0.302	0.0544	$m>o>p$; <i>m</i> small and indeterminate; <i>o</i> , <i>p</i> deactivating
	50	0.159	0.380	0.0200	
	100	0.238	0.449	0.0517	
NH_2 †	0	0.0212	0.0578	(0.0518)	$n>o>p$; all deactivating
	50	0.0363	0.0133	(0.02117)	
	100	0.0538	0.0246	(0.0213)	

* Mononitro series: parent compounds chloronitrobenzenes.

† Dinitro series: parent compounds chlorodinitrobenzenes.

‡ Values throughout in parentheses subject to some uncertainty owing to side reaction or short temperature range used for deriving Arrhenius parameters.

with all three close together and thus easily upset by comparatively minor additional factors. In the range 0–50 °C, which covers the range in which rates are conveniently measurable, the order changes from $p>m>o$ at the lower end to $o>p>m$ at the upper end of the range. It thus appears that both *ortho*- and *meta*-rates are depressed to a slight extent, and this is ascribed to a steric effect in the former case, and both steric and conjugative interactions of Cl and NO_2 groups in the latter. The steric factor in particular is much smaller than the gross effects usually considered.

The OMe can exert a $-I$ effect comparable with that of Cl, but its $+M$ effect is larger. The combined result is then an approximate cancellation of the weaker *I* and second order *M* effects at the *meta*-position, while in the *ortho*- and

para-positions a deactivating influence is expected with a considerable factor favouring the *ortho*-substituent. Neither steric factors nor conjugative interactions between substituents should be able to affect the resultant order $m > o > p$ and this order is found experimentally. The fact that the *meta*-OMe is at all deactivating could be ascribed to second order M effects or the interactions already mentioned. The closeness of the *ortho*- to the *meta*-substituent in activating power is also to be expected.

The NH_2 has a weaker $-I$ and stronger $+M$ effect than either of the other two. Thus even the *meta*-substituent is expected to be deactivating; the *ortho*- and *para*- more deactivating especially the latter. The spacing of the effects is expected to be more even than the OMe, but with the same order $m > o > p$. The experimental results verify these conclusions.

Experimental

Rate constants were measured by estimating base or Cl^- after stopping reaction with dilute HCl or HNO_3 . Either equimolar concn. of aromatic and base or excess base was used, and the values of k_2 obtained graphically. When measuring values at only three temperatures, each was duplicated; for more than three temperatures a minimum of six k_2 -reciprocal temperature values was used to calculate the best values of activation energy E and frequency factor $\log_{10} B$ by the method of least squares. The "probable errors" thus obtained were always less than the estimated errors of ± 200 in E and $\pm 0.1_5$ in $\log B$.

(a) *Typical Kinetic Values.*—A typical run (1,4-dichloro-2,6-dinitrobenzene at 14.0°C) is shown as Table 3, and the full set of rate constants used in calculating the Arrhenius parameters for the same compound shown as Table 4.

TABLE 3
EQUIMOLAR STARTING CONCENTRATIONS ESTIMATING Cl^-

Titration value	..	0.45	0.95	1.39	2.11	2.69	3.12
Reciprocal term	..	44.25	47.79	51.40	58.67	66.20	73.16
Time (hr)	..	0	0.5	1	2	3	4
		3.48	3.79	4.05			
		80.23	87.50	94.71			
		5	6	7			

$$k_2 \text{ (graph)} = 2.00 \times 10^{-3} \text{ l mol}^{-1} \text{ sec}^{-1}$$

$$\text{Least squares} = 2.003 \pm 0.003 \times 10^{-3} \text{ l mol}^{-1} \text{ sec}^{-1}$$

TABLE 4
KINETIC RESULTS FOR 1,4-DICHLORO-2,6-DINITROBENZENE

Temperature ($^\circ\text{C}$)	..	14.0	19.6 ₅	29.4	35.4 ₅
Rate constants ($10^3 k_2$)	..	2.00 2.02	3.53	9.56	16.3 ₅ 16.5

$$\text{Giving } E = 17280 \pm 80 \text{ cal}$$

$$\log_{10} B = 10.46 \pm 0.06$$

(b) *Preparation of Materials*.—2-Chloro-3,5-dinitroanisole, by dinitration of guaiacol, followed by substitution of OH by Cl (Borsche 1917). Recrystallized to constant m.p. from ethanol containing charcoal the product melted at 94 °C (lit. 93–94 °C). 1,4-Dichloro-2,6-dinitrobenzene, by dinitration of *p*-chlorophenol followed by substitution of OH by Cl by the general method of Borrows *et al.* (1949). Recrystallized to constant m.p. from ethanol containing charcoal the product melted at 105 °C (lit. 105–106 °C; 104.9 °C).

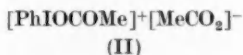
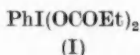
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SOLUTIONS OF PHENYLIODOSO ACETATE*

By W. D. JOHNSON† and N. V. RIGGS†

The ionic nature of diphenyliodonium iodide has been well established by the X-ray investigation of Medlin (1935) and the radioactive iodide ion exchange studies of Juliusburger, Topley, and Weiss (1935), but the position of the so-called iodoso salts is not as clear. Sidgwick and Barkworth (1931) assumed that phenyliodoso propionate contained 3-covalent iodine (I), whereas Sandin (1943) represented phenyliodoso acetate as the ionic structure II in which the iodine is 2-covalent. From the results of conductivity and cryoscopic experiments Zappi and Cortelezzi (1933) concluded that molecular rather than ionic dissociation of phenyliodoso chloride occurred in nitrobenzene or phosphorus oxychloride solution, but this conclusion clearly cannot be applied to the carboxylates.



Phenyliodoso acetate is apparently not appreciably dissociated (or associated) in acetic acid, depression of the freezing point of which is proportional to the concentration of solute in the range, 0.01–0.20M, deviations from linearity being random and not more than 0.01 °C. The slope corresponds to a depression of 3.42 ± 0.06 °C for a molar solution, which may be compared with the molal constant, 3.59 °C, used by Eichelberger (1934); the accuracy of our measurements does not warrant correction for the densities of the solutions. It may

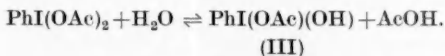
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be remarked however that 1.5 per cent. dissociation at 0.2M into two ions (corresponding to a dissociation constant of 4.5×10^{-5} , ignoring any common ion effect of the solvent) would increase the freezing point depression by only 0.01 °C. The possible presence of ion-pairs is not of course excluded, and it may be noted that Eichelberger (1934) found marked association in acetic acid of the ions of both ammonium nitrate and sulphuric acid at concentrations greater than *c.* 0.05M.

A linear relation also exists between the concentration of phenyliodoso acetate and depression of the freezing points of benzene and nitrobenzene, molar depression constants of 5.9 °C being obtained in each case, which agree approximately with the molal constants (5.1 and 7.1 °C, respectively) quoted in standard texts.

The freezing point of our acetic acid corresponded to the presence of only *c.* 0.03M water, so that significant conversion of solute at the higher concentrations examined to a product (e.g. the hypothetical III) that might not ionize in acetic acid is only a remote possibility; in any case, freezing points of acetic acid solutions of phenyliodoso acetate and up to three molar proportions of water showed depressions corresponding to the total concentration of solute molecules introduced, so that any equilibrium must lie well on the side of the reactants. The fact that phenyliodoso acetate was satisfactorily recrystallized from 50 per cent. aqueous acetic acid is consistent with this view, but favourable differential solubilities may be involved.



The specific conductance of 0.06M phenyliodoso acetate in acetic acid is less than 7×10^{-8} mho at 14 °C, which is not significantly greater than that of the pure solvent (1.4×10^{-8} mho at 25 °C, Eichelberger and La Mer 1933), so that the solute is substantially non-conducting in this solvent. The same conclusion is true for a solution in 50 per cent. aqueous acetic acid in which, because of the higher dielectric constant and greater solvating power, dissociation of ion pairs, if present, is much more likely.

The solubility of phenyliodoso propionate in light petroleum and the behaviour of phenyliodoso acetate as an undissociated molecule in solvents of widely varying polarity and solvating power strongly suggests that these compounds should be represented by covalent structures such as I rather than ionic structures such as II (or the corresponding doubly ionized structure cf. Masson and Hanby 1938). We have observed that the acid residues in phenyliodoso carboxylates are readily exchanged; in view of the above conclusion it is probable that an activated process is involved.

Experimental

Phenyliodoso acetate was prepared by the method of Pausacker (1953). It was recrystallized from glacial acetic acid, washed with ether, and dried over potassium hydroxide pellets in a vacuum desiccator, and had m.p. 162 °C (Found: equiv. wt. (by iodometric titration), 161. Calc. for $\text{C}_6\text{H}_5\text{I}(\text{O}_2\text{CCH}_3)_2$: equiv. wt., 161).

Commercial glacial acetic acid (various samples had m.p. $14.0-16.3^{\circ}\text{C}$) was purified by the method of Orton and Bradfield (1927) and fractionated through 2 ft of Fenske glass helices, the fraction of b.p. $113.5-114.0^{\circ}\text{C}/680\text{ mm}$ which had m.p. $>16.5^{\circ}\text{C}$ (corresponding to the presence of $<0.05\%$ water) being retained as anhydrous acetic acid. Commercial benzene was freed of thiophen by treatment with sulphuric acid in the usual manner and the fraction of b.p. $76-77^{\circ}\text{C}/680\text{ mm}$ fractionally frozen until a sample of m.p. 5.3°C was obtained. Commercial nitrobenzene was steam-distilled from dilute sulphuric acid and the dried product fractionated through 8 in. of glass helices, the fraction of b.p. $134^{\circ}\text{C}/87\text{ mm}$ which had m.p. 5.7°C being retained.

(a) *Freezing Point Experiments.*—A simple Beckmann type apparatus was used since the results of Eichelberger (1934) showed that greater reproducibility is not obtained by the use of much more complex apparatus, and a detailed theoretical treatment of the results was not envisaged in the present work. Anhydrous acetic acid (c. 25 ml) was introduced with a minimum exposure to the atmosphere into the double-walled freezing vessel which was fitted with a rubber stopper carrying a Beckmann thermometer, a bent delivery tube with a stopcock at the lower end, a glass sleeve that fitted a glass stirrer closely and had a side-tube for the introduction of a stream of nitrogen dried by passage through calcium chloride and silica gel to prevent ingress of atmospheric moisture, and a dropping funnel containing c. 0.25M phenyliodoso acetate in acetic acid protected by a calcium chloride drying tube. The freezing vessel was placed in a bath of water maintained at c. 15°C , and its contents stirred while partial crystallization occurred. The thermometer was read when the temperature remained steady for a few minutes, then a portion of solution was added from the dropping funnel and the above operations repeated on the diluted solution obtained. A sample of the solution in equilibrium with solid acetic acid at the observed temperature was siphoned off through the delivery tube (the initial discharge being used to flush the tube and being rejected) its freedom from solid particles established by visual examination, and its concentration determined by iodometric titration. The volume of solution in the freezing vessel was restored approximately from the contents of the dropping funnel, and the series of operations repeated until the equilibrium concentration of phenyliodoso acetate had risen to c. 0.2M . Usually 10 readings were obtained during a run. Some experiments were performed with solvent and solution interchanged, or the methods were used successively, the consistency of the results showing that accumulation of atmospheric moisture was not significant. For example, freezing points (Beckmann thermometer) of solutions of phenyliodoso acetate in acetic acid:

F.p. ($^{\circ}\text{C}$)	5.672	5.420	5.300	5.025	5.100	5.235	5.352	5.450	5.555	5.620
$\text{M} \times 10^2$	0	7.70	11.0	19.1	17.1	13.1	10.0	6.77	3.99	1.92

Slope (least squares) = 3.42 deg mol^{-1} .

Other experiments gave 3.47 , 3.45 , 3.34 deg mol^{-1} .

Measurements in benzene and nitrobenzene were made similarly.

(b) *Experiments in Aqueous Acetic Acid.*—(i) Phenyliodoso acetate was recrystallized from a mixture of equal volumes of acetic acid and water and gave prisms, m.p. 162°C , equiv. wt., 161.

(ii) Freezing point measurements were made as above except that the phenyliodoso acetate was dissolved in acetic acid to which a little water had been added, the amount being determined by a freezing point measurement. It was assumed that pure acetic acid crystallized from the solutions at the freezing points and the concentrations of phenyliodoso acetate and water in the equilibrium solutions were taken as being in constant ratio (determined by titration of the initial solution) during a run. The solutions used contained initially c. 0.1 , 0.2 , and 0.5M water, respectively, and in each case freezing point depressions produced by the two solutes were additive. For example,

Freezing point of anhydrous acetic acid: 4.650°C (Beckmann)

Freezing point of aqueous acetic acid: 2.943°C (Beckmann)

that is water is 0.49M (assuming the linear relation).

The solution added to the anhydrous acetic acid was 0.183M phenyliodoso acetate in this aqueous acid.

F.p. (°C)	4.65	4.47	3.85	3.12	2.77	2.62
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$M \times 10^3$	$\left\{ \begin{array}{l} \text{PhI(OAc)}_2 \\ \text{PhI(OAc)}_2 + \text{H}_2\text{O} \end{array} \right.$	0	1.26	5.80	11.5	14.4	15.6
		0	4.70	22.1	42.9	53.7	58.1

Slope (least squares) = $3.4_s \text{ deg mol}^{-1}$ (total solute).

(c) *Conductivity Measurements*.—A Philips conductivity-measuring bridge, GM4249/07, and cell, GM4221 (constant, 1.47), were used at room temperature (14 °C). The measured resistances of acetic acid and 0.06M phenyliodoso acetate were both beyond the limit of the instrument (10 megohms). A mixture of equal volumes of acetic acid and water had a measured resistance of 900 Ω (specific conductance, 7.5×10^{-4} mho (cf. 7.0×10^{-4} mho at 25 °C, Eichelberger and La Mer 1933) as had 0.006M and 0.016M solutions of phenyliodoso acetate in this solvent.

(d) *Exchange of Carboxylic Acid Residues*.—A solution of phenyliodoso acetate in propionic acid was evaporated at the pump to a syrup from a bath at 60 °C. A cooled solution of the residue in hot light petroleum (b.p. 65–80 °C) deposited clumps of fine needles which, dried in a vacuum desiccator over potassium hydroxide pellets and heated slowly on a micro hot-plate, were observed under the microscope to decompose at c. 50 °C and resolidify; the white solid product was not molten at 210 °C. In a capillary placed in a preheated bath the needles decomposed at 60–65 °C, raised to 67–70 °C by recrystallization from light petroleum (b.p. 55–65 °C). Sidgwick and Barkworth (1931) report the m.p. of phenyliodoso propionate as 67–70 °C from light petroleum. A solution of the needles in acetic acid evaporated as above gave phenyliodoso acetate prisms m.p. 160–162 °C (capillary) from benzene or acetic acid. On the micro hot-plate the acetate decomposed at 155–157 °C and resolidified, the opaque white product not being molten at 210 °C. The decomposition products have not been investigated.

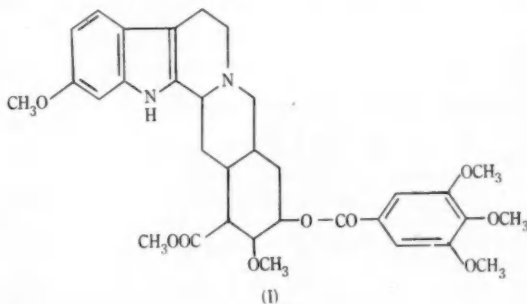
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THE OCCURRENCE OF RESERPINE IN *ALSTONIA CONSTRICTA*
F. MUELL.*

By W. D. CROW† and YOLANDE M. GREET†

In recent years great interest has been aroused in the use of the alkaloid reserpine (I) in the treatment of hypertension and various mental disorders. The roots of *Rauwolfia serpentina* Benth., a member of the family Apocynaceae, from which the alkaloid was originally isolated by Mueller, Schlittler, and Bein (1952), have been used for centuries in India as a sedative, and have been the main commercial source. Further export of this material from India has been banned (Editorial 1955) and although the demand has been partially met by other eastern countries such as Burma, Siam, and Java, and by the use of other reserpine-containing species such as *R. vomitoria* Afz. (Poisson *et al.* 1954) and *R. heterophylla* Roem. et Schult. (Djerassi *et al.* 1953), an intensive search for new sources is being conducted by the pharmaceutical firms concerned in exploitation.



We wish to report the presence of reserpine in the root bark of *Alstonia constricta* F. Muell. ("bitter bark"), a small tree confined to north-eastern Australia and occurring in the Queensland rain-forests. No attempt at complete isolation of the alkaloids has been made, but reserpine has been isolated in approximately 0.05 per cent. yield and identified by comparison with an authentic specimen and by hydrolysis to reserpic acid and 3,4,5-trimethoxybenzoic acid. The results of assays based on the amount of the latter acid produced on hydrolysis of the crude tertiary bases are shown in Table 1. These values cover all alkaloids which produce a non-volatile acid on hydrolysis, but since substantially pure 3,4,5-trimethoxybenzoic acid was produced in each case, rescinnamine (Klohs, Draper, and Keller 1954) was probably absent.

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Deserpidine (Schlittler *et al.* 1955) may be present, but so far only reserpine has been isolated (apart, of course, from known *Alstonia* alkaloids such as alstonine and its congeners). A detailed investigation of the alkaloids of *A. constricta* is in progress and further results will appear in a subsequent paper.

Preliminary tests carried out by the Division of Animal Health and Production, C.S.I.R.O., with the alkaloid from *A. constricta* and authentic reserpine showed general similarity in pharmacological action.

TABLE I
RESERPINE CONTENT OF ALSTONIA CONSTRICTA

Part of Plant	Drying Temperature (°C)	Reserpine (%)
Leaves	60-115*	Trace
Stem bark	60	0.03
Stem wood	60-115	Trace
Mature root bark	60	0.23
Root wood	60	Trace
Small roots	60-115	0.28
Small roots	60	0.26

* Half sample only, remainder dried at 60 °C.

Experimental

All m.p.'s are corrected. Microanalyses were carried out by the C.S.I.R.O. Microanalytical Laboratory.

(a) *Assay Procedure*.—The milled plant material (250-350 g) was extracted with methanol in a Soxhlet for 30 hr, the extract concentrated to remove the methanol, and the residue treated with NaHCO_3 solution and ether. Any resinous material separating at this stage was dissolved in a little methanol and retreated in the same way, this process being repeated thrice or until no more resin formation occurred. All the aqueous solutions were extracted four times with ether and the combined ether extracts washed with 2% acetic acid (3×100 c.c.) then 2% HCl (2×100 c.c.). The combined acid extracts were then basified (NH_3) and exhaustively extracted with ether; any resin formed was redissolved in 2% acetic acid and retreated as already described. The crude tertiary bases obtained on evaporation were hydrolysed by refluxing for 1 hr with 5% methanolic KOH (c. 40 c.c./g), the solvent replaced by an equal volume of water and unhydrolysed bases removed with ether. Acidification and extraction with ether afforded the crude acids which were purified by extraction into NaHCO_3 solution and recovery into ether. Evaporation afforded the pure acids. The percentage reserpine content was calculated from the expression:

$$\frac{287 \times \text{mass of acid}}{\text{mass of plant material}}$$

(b) *Isolation of Reserpine*.—Mature root bark (264 g) was treated as described above up to the stage where the crude bases were obtained in acid solution. Basification with NH_3 gave a resin which would not dissolve in ether. A solution of this material in a little methanol gradually deposited a crystalline precipitate which after several recrystallizations from methanol had m.p. 266-267 °C (Found: C, 65.3; H, 6.9; N, 4.7; MeO, 29.8%. Calc. for $\text{C}_{23}\text{H}_{40}\text{O}_5\text{N}_2$: C, 65.1; H, 6.6; N, 4.6; 6xMeO, 30.6%). Yield 0.07 g. A further quantity was obtained on longer standing. The material did not depress the m.p. of authentic reserpine and the infra-red spectra measured in a "Nujol" mull were identical. The alkaloid had $[\alpha]_D^{20} -116^\circ$ (c, 1.0 in chloroform)

and in an evacuated tube melted at 277–278 °C with subsequent decomposition. Dorfmann, Furlenmeier, and Hueber (1954) quote $[\alpha]_D^{24} -118^\circ$ and m.p. 277–277.5 °C under the same conditions.

Hydrolysis of the alkaloid from *A. constricta* as described in the assay procedure afforded 3,4,5-trimethoxybenzoic acid (m.p. and mixed m.p. with an authentic sample 160–170 °C), and reserpic acid, m.p. 236–237 °C.

The authors are indebted to Mr. L. J. Webb and Mr. J. G. Tracey, Division of Plant Industry, C.S.I.R.O., for collection of the plant material and to Mr. P. Hunter for the extraction work. They wish to thank Dr. J. B. Willis for the infra-red identifications, and Mrs. H. C. Crowley and Mr. L. W. Smith for assistance with the assay work. The pharmacological tests were carried out by the Division of Animal Health and Production, C.S.I.R.O., and the authors are indebted to Dr. A. T. Dick and Mr. J. S. McKenzie for these results.

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OCURRENCE OF SUPININE IN *TOURNEFORTIA SARMENTOSA* LAM.*

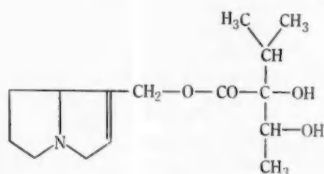
By H. C. CROWLEY† and C. C. J. CULVENOR†

As part of a survey of the Australian Boraginaceae, a preliminary study has been made of the alkaloids of *Tournefortia sarmentosa* Lam., a vine which occurs in north Queensland. The total alkaloid content was small and the crude base was revealed by paper chromatography as a mixture of at least six bases. The assay values given in Table 1 were determined by titration, assuming an average equivalent weight of 300.

TABLE 1
TOTAL ALKALOIDS OF *TOURNEFORTIA SARMENTOSA*

Plant Part			Free Base (% dry wt.)	N-Oxide (% dry wt.)
Leaves	0.017	0.048
Stems	0.057	0.12

The major component of the crude base from both leaf and stem had R_F 0.37 and crystallized readily from acetone. It proved to be identical with supinine (I), first isolated from *Heliotropium supinum* (Menshikov and Gurevich 1949) and occurring also as a minor alkaloid in *H. europaeum* L. (Culvenor



(I)

1954). Determination by partition chromatography showed the supinine content (base + *N*-oxide) to be 0.04 per cent. in the leaves and 0.15 per cent. in the stems. In both cases, it exists predominantly as the *N*-oxide. Identification of the other constituents was not possible with the small amount of material available.

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Experimental

(a) *Estimation of Total Alkaloid*.—Milled plant material (collected near Tully, north Queensland, in November 1951; leaves 480 g, stems 553 g) was extracted with methanol and the methanol distilled from the extract under reduced pressure. The residue was extracted with dilute HCl and of the resulting aqueous solution 10% was reserved and the remainder was reduced with zinc dust. Both reduced and unreduced portions were then made alkaline with ammonia and extracted with chloroform. The crude base fractions thus obtained were made up in methanol solution to standard volumes, and aliquots were evaporated and titrated with *p*-toluenesulphonic acid in chloroform. Results, calculated on the assumption of an average equiv. wt. 300, are given in Table 1.

(b) *Isolation of Supinine*.—On a paper chromatogram developed with butanol-acetic acid, both the reduced and unreduced base fractions showed spots of R_F 0.61 (faint), 0.57, 0.50, 0.37 (strong), 0.25, and 0.09. The base from the leaf also showed a faint spot of R_F 0.18. Supinine has R_F 0.37.

Crystallization from acetone of the reduced base from the stems gave supinine (0.42 g), m.p. and mixed m.p. 147–148 °C, $[\alpha]_D^{18} -13^\circ$ (c, 2.01 in ethanol) (Found: C, 63.7; H, 9.0; N, 5.2%. Calc. for $C_{14}H_{25}O_4N$: C, 63.6; H, 8.9; N, 4.9%). The sample isolated from *H. europaeum* had m.p. 148–149 °C, $[\alpha]_D -12^\circ$ (ethanol).

The residual crude reduced base was run on an assay partition column (Culvenor, Drummond, and Price 1954) to determine the total amount of supinine present. No other crystalline substance could be obtained from the titrated eluate fractions. The stems were found to contain 0.15% and the leaves 0.04% of supinine (including that present as *N*-oxide).

The authors are indebted to Mr. L. J. Webb, C.S.I.R.O., for the collection of plant material.

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CORRIGENDUM

Volume 8, Number 2

Page 273, line 3 and 1st footnote to Table 3, line 2: *For* (53% w/v) *read* (53% w/w; sp. gr. 1.127).



